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# GEOCHIMICA ET COSMOCHIMICA ACTA



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# The nickel content of deep-sea deposits

Hans Pettersson and Henri Rotschi

*(Received 12 April 1951)*

ABSTRACT

Determinations of the nickel, manganese and iron present in sediment cores from the Central Pacific Ocean have been made by microchemical methods. The results show (a) that the nickel content is high relative to that of continental rocks and sediments and, (b) that there are considerable variations in the nickel contents with depth below the sediment surface. No correlation with the manganese and iron contents is evident except in cases where a change in the rate of sedimentation appears to have affected all three elements in the same manner.

It is tentatively suggested that this abundance of abyssal nickel may be partly derived from cosmic dust settling over the earth's surface. Arguments for and against this thesis are put forward.

This paper* sets out the results so far obtained in determinations of nickel, manganese and iron in deep sea sediment cores. They have been made partly in the Oceanography Institute, Göteborg and partly in the Geochemical Laboratory of the Swedish Geological Survey (S.G.U.) in Stockholm by Dr. S. Landergren. Although the paper deals primarily with the nickel content which affords points of special interest, the iron and manganese contents are included for purposes of comparison. Iron and manganese are components of red clay and radiolarian ooze but opinions differ regarding their origin and the occurrence of these two elements will be dealt with in a later report [1].

Little has been published on the occurrence of nickel in deep-sea deposits. The earliest reference known to the writers appears in the "Challenger" Reports, vol. 4, Deep-Sea Deposits by Sir John Murray and the Rev. A. D. Renard [2]. Their analyses show only traces of nickel in a few of the sediment samples but in manganese nodules taken from great depth traces of nickel were not unusual. Indications of cobalt were more rare.

The lack of precise data is not surprising considering the low sensitivity of the methods used for determining the nickel content fifty years ago. In the second decade of this century very sensitive microchemical methods for measuring small quantities of nickel by means of colour reactions came into use. By means of colourimetric determinations on an organic nickel compound with the Pulfrich spectrophotometer it is fairly easy to measure quantities of the element as low as a few parts per million.

These modern methods have so far been used chiefly for measuring the nickel in continental rocks and sediments. The only nickel determinations on deep-sea deposits recorded during the present century are those by Clarke and Steiger [3]. In a composite sample made up from 51 varieties of red clay from different localities the content was found to be 0·032 % of nickel oxide or 0·025 % of the element. This figure is considerably higher than the average value of 0·008 % Ni given by Sandell and Goldich [4] for the uppermost crust of the earth.

* A full report will appear in the series "Report of the Swedish Deep-Sea Expedition" to be published by the Royal Society of Göteborg.

No explanation has so far been suggested for the origin of this abyssal nickel. A fairly constant supply of nickel should give high values in sediments, such as red clay and radiolarian ooze, which have a slow rate of accumulation. Four sources of nickel seem worthy of consideration:

*1. Directly from the land area*—Terrestrial material in the form of wind- and / or water-borne particles of very small size, such as the finest clay particles from rivers, desert sand is carried seawards by the winds, or ash from continental or island volcanoes. The nickel content of this material is not likely to be appreciably higher than that of similar material hitherto analysed and therefore a much higher content in deep-sea deposits presupposes a concentration *in situ* by some submarine process by which other components are dissolved leaving the nickel in a more concentrated state.

*2. From the sea water*—The nickel content in ocean water according to Ernst and Hoermann [5] is extremely low, being in the order of 0·1 $\gamma$ per litre. This figure is approximately 500 times less than the average for iron. The extraction of nickel by marine organisms has not been observed.

*3. From magma, erupted onto the sea bottom*—If this magma contains a higher concentration of nickel than that found in ordinary rocks or sediments on the continents then this may be a sufficient source of the element. The numerous volcanic islands of the three oceans, and especially of the Pacific, establish that volcanic eruptions on a large scale occur in great ocean depths. Submarine lava beds of considerable size were observed on the "Albatross" cruise both in the Pacific and Indian Oceans [6].

*4. Extra-terrestrial sources*—Meteoric dust settling from shooting stars and dispersed in the higher atmosphere, or unchanged minute particles from interplanetary space; the micro-meteorites of Öpik and Whipple [7] and [8], provide a source of nickel. The proportion of extra-terrestrial nickel in the deep-sea deposits can be expected to vary, in general, in inverse ratio to the rate of sedimentation and therefore to rise to a maximum in abyssal sediments having a very low rate of accumulation. On the other hand, such an accrument of cosmic nickel is likely to show local variations due to the incidence of exceptionally heavy meteor showers. (Compare Nininger [9].)

If an extra-terrestrial origin for a considerable, if not the major part of the nickel in red clay and radiolarian ooze is admitted, then large variations of the nickel content along the length of a deep-sea core may be interpreted as indicating significant variations, either in the rate of sedimentation or in the rate of accumulation of meteoric dust and micro-meteorites or perhaps both. These variations would thus depend on the cosmic history of our earth or of the solar system to which it belongs.

This latter suggestion gives a particular interest to the study of abyssal nickel. It seems possible that the rate of accumulation of the supposedly cosmic material, as far as can be determined from measurements of the absolute rate of sedimentation, may afford a check on the accuracy of the conclusions reached by astronomers from meteor counts and estimates of the quantity of cosmic dust in interplanetary space based on the strength of the zodiacal light, a problem in which students of solar radiation and its variations with time are greatly interested [10].

## Results of the Analyses

Sandells [11] method was used for the nickel determinations. It is based on the brown colour obtained when dimethyl-glyoxime is added to an alkaline solution containing nickel which has been treated with an oxidizing agent. Large quantities of aluminium interfere with the colour reaction and manganese, readily oxidized to its dioxide, also gives a brown colour. Iron gives a yellow colour with the citrate which was used. Due to the above complications it was necessary to extract the nickel by utilizing the solubility of the complex nickel-dimethylglyoxime in chloroform in a slightly alkaline solution, a method also recommended by Sandell. By this technique it was possible to measure quantities of nickel considerably less than 10 $\gamma$ by means of the Pulfrich photometer when using quantities of the sample which contained amounts of nickel between 5 $\gamma$ and 50 $\gamma$.

Identical solutions from the samples were used for determining the iron and manganese contents. Iron was estimated by utilizing the red colour produced when potassium thiocyanate is added to an acid solution which has been treated with an oxidizing agent. Oxidation to the permanganate with ammonium persulphate was used for the manganese determinations. This method has been described in detail by F. Nydahl [12].

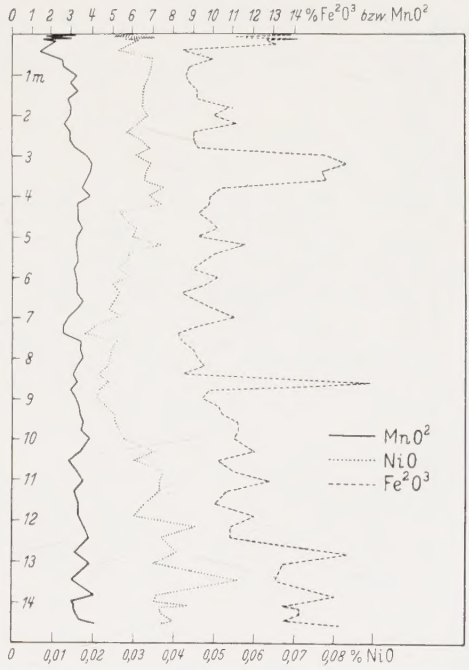


Fig. 1. Core 72.

The first determinations were made on two long cores of red clay taken close together at Albatross Station 105 (Lat. S 7° 38′, Long. W 152° 53′, depth 5000 m) about 1000 nautical miles north of Tahiti. A cursory examination, made on board the ship, showed the deep chocolate brown sediment to be homogeneous. The content of siliceous and calcareous organic remains was low.

The results, which are shown in Fig. 1, varied from a minimum for NiO of 0·041 % at 742 cm below the top of the core to a maximum of 0·089 % at 862 cm. Five distinct maxima of NiO occurred at sediment depths of 322, 862, 1280, 1387, and 1457 cm.

The iron content varied between 3·60 % and 11·17 % $Fe_2O_3$ and the manganese between 1·38 % and 4·14 % $MnO_2$. Apart from a minimum for all three oxides at 742 cm no correlation between the variations is evident from the curves.

The average values from the 77 samples were: NiO—0·056 %; $Fe_2O_3$—6·21 %; $MnO_2$—3·13 %. The average nickel value is almost twice as high as that found by

Clarke and Steiger for their composite sample of red clay and the maximum value nearly three times their average.

After publishing these results in a letter to Nature [13] work was resumed in the Autumn of last year on other cores from the central Pacific Ocean. The following is a summary of the results:

*Core 69*—Albatross Station 102 (Lat. S 13° 25′, Long. W 143° 30′, depth 4625 m). A red clay rich in phillipsite crystals and homogeneous in the uppermost 3 m with an increase in lime in the lower parts. Average contents were: NiO—0·029 %; $Fe_2O_3$ 7·83 %; $MnO_2$—2·69 %. At 222 cm below the top of the core there were two maxima of NiO close together, 0·098 % and 0·064 % respectively, with an intermediate minimum in a thin layer apparently of volcanic origin (0·048 % NiO). Below the 300 cm level the sediment becomes richer in lime with a maximum of 60 % whereas the nickel, manganese and iron contents fall off due to the diluting effect of the calcareous remains. Recalculating the values for a sediment free of lime the three curves are found to be independent of each other except for a common minimum at 480 cm.

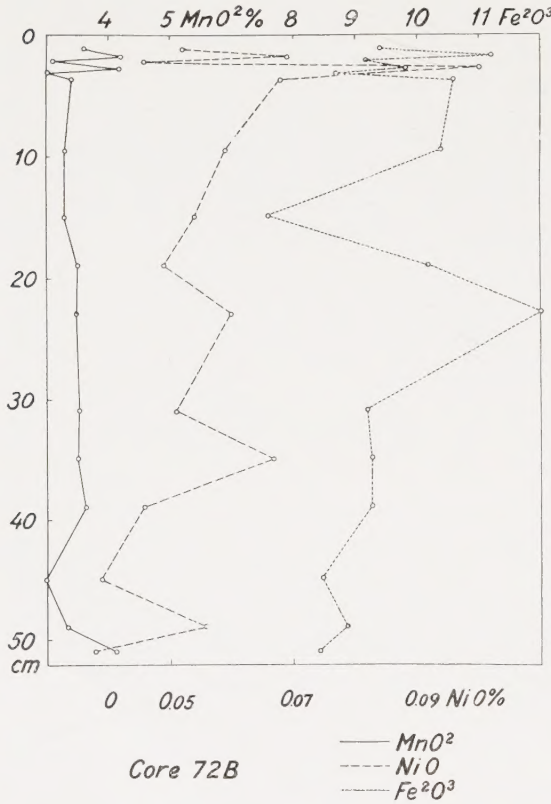


Fig. 2.

*Core 70*—Albatross Station 104 (Lat. S 11° 15′, Long. W 150° 30′, depth 4920 m). A red clay with a low lime content but rich in phillipsite. Average contents were: NiO—0·036 %; $Fe_2O_3$—9·38 %; $MnO_2$—3·24 %. The nickel content was fairly constant with a slight maximum of 0·047 % at 120 cm. The nickel and manganese variations are similar but the iron decreases with depth from a high content in the uppermost portion.

In addition to the long cores described above analyses were carried out on some short cores which were taken by a different technique. In these cores the uppermost surface layer is preserved whereas in the long cores a top layer varying from a few centimetres to ten or more centimetres may be missing. One of these cores, taken at the same locality as core 72 and designated as 72 B, had a length of 56 cm (Fig. 2). The averages from a length of 49 cm were NiO—0·058 %, $Fe_2O_3$—9·54 %, $MnO_2$—3·52 %. Immediately below the sediment surface this core had a maximum of 0·10 % NiO which was the highest observed in any of the cores. On the other hand, short cores taken north of the Equator somewhat further east gave considerably lower values for nickel and manganese. Core 77 B (Fig. 3) (Lat. S 9° 30′, Long. W 148° 40′, depth

5360 m) was poor in lime and rich in radiolarians and had average contents of only 0·009 % Ni, 0·42 % $MnO_2$ and 6·50 % $Fe_2O_3$. The composition of the uppermost 10 cm of the core was extremely variable. The dilution effect due to the silicious remains was evident and the high iron content was remarkable.

Similar results were noted with other short cores, taken between the Equator and Hawaii, which were rich in radiolarians (Fig. 4). Here also low values of nickel and manganese were found.

It is of interest to compare the nickel, manganese and iron contents by calculating the average Mn : Ni and Fe : Ni ratios for each core (Table 2). The Mn/Ni ratio for typical radiolarian ooze is fairly constant between 33 and 41, the same as in cores 72 and 72B, but in cores 69 and 70 it rises as high as 75 and 73.

A few cores which were rich in lime were analysed by Mag. Bauer in the *Oceanographic Institute*, Göteborg. As a result of the dilution by calcareous remains (up to 90 % of the total weight) the nickel content was only a few parts in a hundred thousand and the Mn/Ni ratio was as low as between 13 and 20.

Recalculating the data from these cores for a non-calcareous sediment the nickel and iron values were about as high as those in core 72 but the manganese content is fairly low (three to five times less). The Mn/Ni ratio for red clay is much higher (45–75) and for globigerina ooze much less (13–20). The Fe/Ni ratio was still more variable: from 100 to 250 for red clay; from 190 to 650 for radiolarian ooze; from 68 to 220 for globigerina ooze.

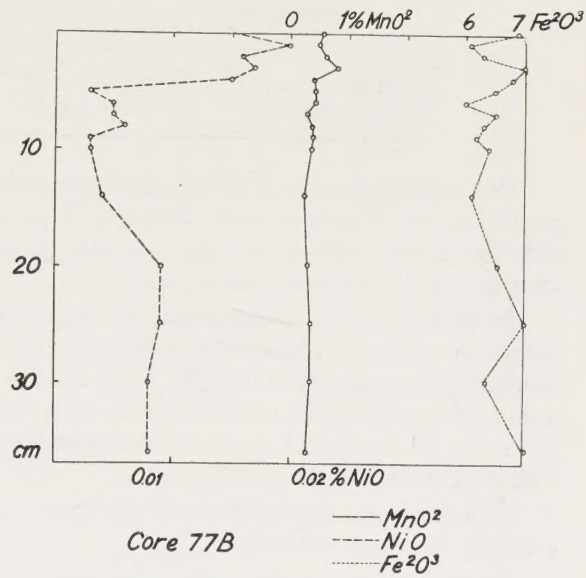


Fig. 3.

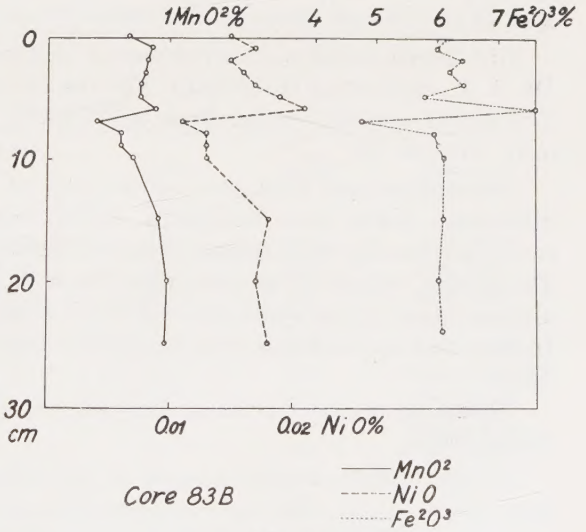


Fig. 4.

Preliminary experiments were carried out to ascertain the nickel content in grains of different size. After the magnetic particles were extracted from the sediment of core 72 between depths of 1360 and 1410 cm a large volume of material was available for further investigations. This residue was submitted to a mechanical separation into fine particles with an equivalent diameter of 0·003 mm and larger

particles exceeding 0·006 mm. The results of the determinations on this material was as follows:

| *Particle Size* | NiO % | $MnO_2$ % | $Fe_2O_3$ % |
|---|---|---|---|
| Less than 3 μ . . . . . | 0·064 | 4·25 | 10·90 |
| Greater than 6 μ . . . . | 0·026 | 1·05 | 3·23 |

One explanation for the concentration of nickel, manganese and iron in the finest particles may be the greater adsorption power of the latter. Another explanation (limited to the nickel and iron content) might be the preponderance of nickel and iron in highly disperse cosmic dust.

In view of the possibility that the nickel in the deep-sea sediments may have its origin in magma extruded over the ocean floor, at the suggestion of the writers, analyses of magmatic material were kindly undertaken by Dr. LANDERGREN. He analysed a number of representative samples for their content of nickel and other elements by means of a precision spectrographic method he has developed. The following were investigated:

(i) A fragment broken from a submarine lava bed in the eastern Pacific Ocean at a depth of nearly 4100 m.

(ii) Two specimens of basaltic rock obtained from the bottom of the Indian Ocean at a depth of nearly 3400 m by the John Murray Expedition. (Given by Dr. J. WISEMAN of the *British Museum of Natural History*, London.)

(iii) Three samples of supramarine basalt from Hawaiian volcanoes. (Given by Dr. J. T. JAGGAR of Honolulu.) The results of these analyses are shown in Table 1. The nickel content varied from 0·005–0·012 % Ni. The submarine lava contained only 0·006 % Ni.

Determinations were also carried out on the nickel content of some basic and ultra-basic rocks from Nukuhiva, Tahiti and Oahu, on the assumption that such rocks, supposedly from deeper layers of the earth's crust, may be fairly rich in nickel. The results, which are shown in the lower part of Table 1, show that in one case (an olivine basalt from Mahaena in Tahiti) a nickel content of 0·13 % NiO was found. In the other rocks of this type the nickel content varied between 0·002 % and 0·018 % NiO.

Summing up the results of the analyses set out in the preceding pages it may be stated that:

1. The nickel content in most of the cores so far investigated was much higher than the average value for continental rocks and sediments with maximum values ten times higher than the continental average. The highest nickel values were found in material with a low rate of sedimentation (in the order of 1 mm in 1000 years). The lower values observed appear largely due to the dilution effect of calcareous or siliceous microfossils. Variations in the nickel content with depth below the sediment surface are conspicious, especially in long cores of red clay and radiolarian ooze, with maxima two to three times higher than the average value found for the same core.

*Table 1. Spectrographical analyses**

| | *Position* | *Depth m* | Ni % |
|---|---|---|---|
| | *Submarine material* | | |
| Lava | 11° 25′ N, 113° 48′ S | 4090 | 0·007 |
| Variolitic basalt | 1° 25′ S, 66° 34′ E | 3385 | 0·005 |
| Basalt with augite and oligoclase | 1° 25′ S, 66° 34′ E | 3385 | 0·01 |
| Variolitic augite basalt | 1° 25′ S, 66° 34′ E | 3385 | 0·006 |
| Hornblende augite dolerite | 1° 25′ S, 66° 34′ E | 3385 | 0·006 |
| Basaltic fragment | 6° 55′ N, 67° 10′ E | 4793 | 0·012 |
| Olivine augite basalt | 8° 35′ N, 94° 10′ E | 2268 | 0·01 |
| | *Supramarine material* | | |
| Basalt | Oahu | | 0·019 |
| Basalt | Hualalai, Hawaii | | 0·022 |
| Basalt | Hualalai, Hawaii | | 0·012 |
| Old pitchstone | Puu Waawaa | | $\leq$ 0·001 |
| Old pitchstone | Puu Waawaa | | $\leq$ 0·001 |
| | *Microchemical analyses*** | | |
| Laterite | Pali Oahu | | 0·014 |
| Laterite | Moku au Toto, Nukuhiva | | 0·009 |
| Basalt | Taipi Vai, Nukuhiva | | 0·014 |
| Volcanic Glasses | Nukuhiva | | 0·001 |
| Basaltic lava | Tenua kue Nui, Nukuhiva | | 0·013 |
| Olivine-basalt | Mahaena, Tahiti | | 0.10 |
| Pyroxenite | Mahaena, Tahiti | | 0·014 |

* By Dr. Landergren. ** By Dr. M. Rotschi.

*Table 2*

| *Core* | NiO % | $F_2O_3$ % | $MnO_2$ % | Mn/Ni | Fe/Ni | *Sediment* |
|---|---|---|---|---|---|---|
| 69 | 0·029 | 7·83 | 2·69 | 75 | 250 | Red clay |
| 70 | 0·036 | 9·38 | 3·24 | 73 | 235 | Red clay |
| 72 | 0·056 | 6·21 | 3·13 | 45 | 100 | Red clay |
| 77 B | 0·009 | 6·51 | 0·42 | 40 | 650 | Rad. ooze |
| 83 B | 0·016 | 6·11 | 0·76 | 37 | 330 | Rad. ooze |
| 85 B | 0·021 | 5·99 | 1·04 | 41 | 260 | Rad. ooze |
| 86 B | 0·022 | 4·69 | 0·87 | 33 | 190 | Rad. ooze |
| 87 B | 0·020 | 4·57 | 0·98 | 39 | 200 | Rad. ooze |
| 75 | 0·006 | 0·46 | 0·13 | 17 | 68 | Glob. ooze |
| 93 | 0·008 | 1·04 | 0·12 | 13 | 120 | Glob. ooze |
| 95 | 0·004 | 0·93 | 0·1 | 20 | 220 | Glob. ooze |

2. The iron and manganese contents determined in the same samples also displayed considerable variation with depth. In general, however, these do not run parallel to those for nickel except in some of the short cores (especially manganese). The cause in the few cases where coincident maxima were found for nickel, iron and manganese is probably due to changes in the rate of the sedimentation and dilution effect. The Mn/Ni ratio varied from less than 20 to over 70, with an average of

approximately 45 which in not far from the ratio between the two elements assumed to prevail in seawater. The Fe/Ni quotient varied between 70 and 650 with an average of 200, whereas the ratio in seawater is about 500. Core 93, which was extremely rich in forams, was a rather exceptional case. The Mn/Ni ratio was as low as 13 but the Fe/Ni ratio was 120 and therefore much closer to the average value. Possibly the abundance of calcium of organic origin in the sediment has counteracted the accretion of manganese or has facilitated its disappearance through resolution.

3. Consideration of the above-mentioned sources of nickel as a means of explaining the high nickel content of deep-sea sediments, and especially those having a low rate of accumulation, led the writers to the conclusion that it was improbable that it was due to terrestrial material in the form of wind or waterborne particles because of their original very low nickel content. The same objection applies to a magmatic source from lava ejected over the ocean floor. Both these sources presuppose an extraction process operating in the bottom water, by which the greater part of the matrix becomes dissolved, leaving the nickel in a state of 5- to 10-fold concentration. A magmatic origin would require periodic outbursts of lava especially rich in nickel in order to account for the variation found in the distribution of the element along cores of great length. In view of the present imperfect knowledge of the chemical processes operating on the ocean floor neither hypothesis can be considered impossible. A more detailed study of the content of other elements present in the deposits may yield more conclusive evidence for or against these explanations.

The very low content of the element has already been cited as an objection to the sea-water as a source of the abyssal nickel. On the other hand it must be admitted that the Mn/Ni ratio in some of the cores approaches that assumed to exist in seawater and this lends some support to this theory, for the abyssal manganese is in all probability largely derived by a percipitation and/or adsorption process. The fact that the variations found in the nickel content with depth below the sediment surface do not show any close relationship with those of manganese would seem to refute this explanation. In any case, the adsorption or precipitation process leading to the deposition of nickel must be different from that by which manganese is deposited.

The surprisingly large amounts of nickel found in the sediments of the central Pacific Ocean at first consideration seem to contradict the suggestion that the element is of cosmic origin and derived from meteoric or cosmic dust from interplanetary space. Core 69 may be taken as an example. The average content of NiO in the uppermost 10 cm was 0·051 % or 0·040 %–Ni. The fresh sediment has a specific gravity of 1·5 and contains 65 % seawater and thus the nickel contained in one cc. of the sediment is $200 \times 10^{-6}$ g. By means of a detailed radium analysis of the top layers the rate of sedimentation was found to be 0·04 mm in 1000 years. The accumulation of nickel in this time would be $8 \times 10^{-8}$ g per $cm^2$ of the bottom surface. It is assumed that this nickel remains stationary in the sediment.

Assuming that *the whole* of this nickel is of cosmic origin and that the distribution is uniform within the time-span involved, the total accumulation of the element to the whole surface of our planet becomes $40 \times 10^{12}$ g per 1000 years or 40000 tons per annum. Ascribing an average nickel content of 2 % to the cosmic dust, the latter figure has to be multiplied by 50 in order to reach the total contribution of extraterrestrial matter to the earth in the course of one year which gives

2000000 tons*. Comparing this figure with that of 1800 tons which was derived from meteor counts according to WATSON, the difference seems disconcerting for the cosmogenic hypothesis.

It was therefore thought desirable to submit the results to authorities on meteors and cosmic dust from interplanetary space. Dr. F. WATSON, in a private communication to one of the writers, states that for various reasons, the figure based on meteor counts can only be taken as a lower limit for the amount of material actually deposited on the earth's surface, and that the true figure may well be higher by one, or even two, powers of ten. Dr. F. WHIPPLE, of the Harvard Observatory, very kindly sent the writers a typescript copy of an unpublished paper on "The theory of micrometeorites." In this paper he discusses the possibility of very small particles, a few $\mu$ or less in diameter, penetrating the atmosphere and being deposited on the earth without being heated to incandescence by aerial friction. Dr. WHIPPLE expresses the opinion that the total mass of these invisible micrometeorites may be 10000 times greater than that of the visible meteors. Dr. ÖPIK, of the *Armagh Observatory* in N. Ireland and formerly of the *University of Tartu* and the *Harvard Observatory*, had noticed the results published in a letter to Nature and had the kindness to send the writers a typescript copy of a new paper. In this most interesting work, Dr. ÖPIK discusses the total quantity of cosmic dust present in interplanetary space and which is responsible for the zodiacal light. He concludes, from his calculations, that the total quantity of such dust swept up by the earth approaches the value obtained from this study of the nickel in deep-sea deposits and may, with certain assumptions on the composition of this dust, give very close agreement. Dr. ÖPIK, in a personal communication to one of the present writers, stresses the astronomical importance of this research on the deep-sea deposits and the desirability of it being extended to still more material.

These converging opinions from three authorities on meteors and interplanetary dust encourage the view that the main part of the nickel discovered in the deep-sea sediments may be of cosmic origin. Dr. ÖPIK feels that the very considerable variations in the nickel concentrations along the longest cores (Nos. 71 and 72) are more difficult to explain. The above mentioned paper by Dr. ÖPIK deals with these difficulties in detail.

Dr. LANDERGREN, on the other hand, in a recent paper on the results of spectrographic analyses of samples from one of the long "Albatross" cores collected in the Romanche Deep (Lat. S 00° 13′, Long. W 18° 26′, depth 7500 m) where considerable variations in the nickel content were found, expresses the opinion that the nickel may be of terrestrial origin.

* It has been assumed in these calculations that *all* the nickel found in abyssal sediments is of cosmic origin in order to obtain a maximum value for the accumulation of the material required. Obviously this assumption cannot be correct for a considerable part of the nickel is probably of terrestrial origin. Assuming an average of 0·015%–NiO for terrestrial material and deducting this from the 0·051%–NiO found in the top part of core 69 means that the remaining two-thirds or 0·036% would be the net contribution of NiO from extra-terrestrial sources. This would reduce the total quantity of such material carried to the earth from 2000000 tons to 1400000 tons annually. If a further increase in the terrestrial nickel occurs as a result of secondary processes such as solution, adsorption, etc., a further reduction in the cosmic material is possible. It seems, however, that the maxima of the nickel content, unparalleled by similar maxima in the manganese and iron values, are probably of extraterrestrial origin and consequently of special interest.

One critical experiment which suggested itself was that of analysing red clay samples which were rich in nickel for elements of the platinum group and especially platinum and palladium*. The average platinum content in iron meteorites according to Goldschmidt should be 20 g per ton and of palladium 10 g per ton, whereas in continental rocks the values are about 10000 times less. In stony meteorites also, the two elements are much less concentrated in relation to nickel.

Dr. Harrison Brown of the Institute for Nuclear Physics in Chicago has kindly undertaken to analyse some of the samples for palladium after activation in the neutron pile. It is therefore possible that the question of the absence or presence of platinum metals in a concentration indicative of a cosmic origin may be settled in the near future.

In the meanwhile this investigation is being continued on cores from the Western Pacific Ocean and also from the two other oceans.

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* A qualitative test for platinum and palladium was undertaken by Mag. Bauer with negative results.

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# The brecciated stony meteorites and meteorites containing foreign fragments

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ABSTRACT

It is pointed out that the breccias among stony meteorites are mainly of two kinds: (a) breccias in which the enclosed fragments are of the same material as the surrounding principal mass of the stone: it is proposed to call this kind of breccias "*monomict breccias,*" and (b) breccias in which the enclosed fragments are of a foreign material as compared with the surrounding principal mass of the stone: it is proposed to call these breccias "*polymict breccias.*"

The brecciated stony meteorites have so far been only superficially studied. In the present investigation it is shown that the occurrence of "monomict breccias" is mainly limited to various kinds of "achondrites," whereas "polymict breccias" occur among the achondrites (*e.g.* all Howardites are polymict breccias) as well as among the chondrites.

A petrographic investigation of thin-sections of a great number of fragments contained in the different kinds of stony meteorites, shows that most stony meteorites, achondrites as well as chondrites, and also a number of types not known as yet as separate meteorites, occur as fragments in "polymict" brecciated stony meteorites. This remarkable result of the investigation shows that rocks made up of most kinds of stony meteorites must have existed on the cosmic body where these polymict breccias were formed; and the investigation thus throws light on the origin of the stony meteorites.

## Introduction

It has early been observed that a great number of the stony meteorites have a brecciated structure. The brecciation has even been used in classifying the different groups of stony meteorites. Thus Brezina has taken the occurrence of brecciation and of veins as a basis of classification, and has divided most kinds of stony meteorites into ordinary, veined and brecciated, using for instance the symbols Cw for "white chondrites," Cwa for "veined white chondrites" and Cwb for "brecciated white chondrites." It is therefore surprising that these meteoritic breccias have not been more closely investigated and described. Usually only the fact of their occurrence is mentioned.

From old records we have, however, a few descriptions which are worth mentioning here. In his catalogue—from the year 1843—of the Vienna collection, Partsch [1] speaks of brecciated structures approaching those exhibited by marbles ("Marmorierung"). In 1860 v. Reichenbach [2] published a remarkable paper on "Meteoriten in Meteoriten" which contains a wealth of observations of great importance with regard to the deciphering of the genesis of stony meteorites. That only little attention has been paid to this paper is perhaps explained by the circumstance that v. Reichenbach did not distinguish between the angular fragments enclosed in brecciated stones and the chondrules and fragments of chondrules contained in the stones. He even went so far as to consider every spherical chondrule as a separate small meteorite enclosed in the ground-mass of the stony meteorite with which he was dealing. Hence the importance of his remarks with regard to the fragments different from the main mass in which they were enclosed was obscured. It is noteworthy that v. Reichenbach in this same paper describes "schistose structures" and "stratification" which he had observed in no less than thirteen meteorites.

In 1861 and 1863 Haidinger published some observations on brecciated structures in Parnallee [3], [4], [5] and in 1869 on related structures in Rutlam (= Pulsora) [6]. Also Story-Maskelyne [7] in 1863 described the brecciated structure of Parnallee. The most interesting accounts of Parnallee have been published by Stanislas Meunier [8], [9], who in 1871 and 1884 described seven different kinds of meteorite fragments as enclosed in the principal grey mass of the meteorite. Meunier points out that an analysis of such a stone in reality represents an analysis of a large portion of a grey chondrite to which pieces of different kinds of meteorites have been added, and does not represent the composition of any particular type of stony meteorite. But with regard to the enclosed fragments, which we could designate "foreign fragments," Meuniers descriptions are also somewhat scanty; they represent an enumeration and classification rather than a description of these fragments.

In his important work "Die mikroskopische Beschaffenheit der Meteoriten erläutert durch photographische Abbildungen" Tschermak [10] 1883–1885 in the text accompanying the figures briefly mentions the brecciated structures of stony meteorites, giving as examples the stones of "Shytal," "St. Mesmin" and "Pulsora." In conclusion he makes the following general remark with regard to the brecciated structures: "Von der deutlichen Breccienstruktur bis zum gleichartigen Aussehen gibt es alle Übergänge, die angeschliffen entweder bloss feine dunkle wirr verlaufende Linien oder aber eine wolkige Zeichnung, endlich ein marmoriertes Aussehen darbieten."

In describing the structures of stony meteorites Cohen [11], makes some brief remarks with regard to the structures, "die als breccienähnliche, teils direkt als Breccienstruktur bezeichnet wird . . ." He makes some references to the opinions published by Haidinger and Meunier, mentioned here earlier, and sums up his remarks by giving his own opinion as follows: "Da ich das breccienähnliche Aussehen nur für eine 'Pseudotrümmerstruktur' halte, nehme ich an, daß zwischen den beiden Strukturformen keinerlei genetische Beziehung besteht." The failure of Cohen—the greatest authority on meteorites of his time—to recognize the importance of the breccia structures of stony meteorites has perhaps been the reason why these structures from the time of Cohen and later have been so little dealt with in the literature on meteorites.

A certain number of petrographic descriptions of the foreign fragments contained in stony meteorites have, however, been published since then. The following may be briefly mentioned here, as they will be discussed in more detail later. In 1906 the present author [12] petrographically described a number of different kinds of fragments separated from the howardites of Luotolaks and La Vivionnère, of which fragments he had managed to prepare thin-sections. Many of these fragments are typical "eucrite" pieces, some of which show alterations caused by more or less far-reaching heat action (partial melting of the components). Some of the fragments studied, however, represent meteorite species not hitherto observed as separate meteorites. These will be more closely described somewhat later.

Merrill has described several meteorites in which angular fragments of a material different from that of the principal part of the stone have been found, and has also published pictures of these. Especially the publications on "Cullison" [13], "Weston" [14], "Cumberland Falls" [15] and "Plainview" [16] should be

mentioned. The most sensational of these instances is the achondrite of "Cumberland Falls," consisting of a "Chladnite" (= white enstatite stone) in which fairly large angular pieces of a "black chondrite" (of the Farmington type) and also some small fragments of graphite are embedded; of this we possess a good description by MERRILL, together with some beautiful pictures [15]. A reproduction of one of the pictures of this remarkable stone is given here (Figure 1). Figures 2 and 3 show white and black fragments contained in the grey chondrite of "Hainaut" [32]. "Plainview" again is an example of such breccias which during one or several subsequent stages of their cosmic history have been more or less strongly heated and subject to a "thermometamorphism," whereby a far-reaching recrystallization and obliteration of the originally sharp borderlines of the fragments in the breccia has taken place, resulting in what the early authors called a "marble structure."

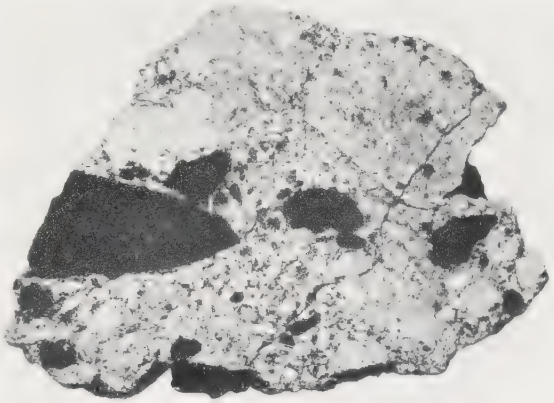

Fig. 1. Polymict breccia.
Chladnite from "Cumberland Falls." $\frac{1}{2}$ size.

Fig. 2. Meteorite of "Hainaut." "Polymict breccia." Fragments of "White chondrite" enclosed in "Grey chondrite." $\frac{3}{4}$ natural size.

### DIFFERENT KINDS OF BRECCIAS

#### *"Monomict" and "polymict" breccias. Unaltered and metamorphosed breccias*

Among the stony meteorites, especially the "achondrites," there are a great many brecciated stones containing only fragments and pieces of the *same material* as the principal mass of the stone. Examples of such breccias are found in most of the "eucrites," where portions of the stone (Juvinas) or the greater part of the stones (Peramiho, Stannern) have been crushed and brecciated. In another group of brecciated stones, as examples of which the already mentioned stone of "Cumberland Falls," most of the howardites, howarditic-chondrites and many other kinds of chondrites may serve, we see fragments of an entirely different kind embedded in the main mass of the stone. *Often these fragments differ among themselves and it is evident that here we have to deal with a kind of accumulation breccia.* These two principal kinds of meteorite

breccias will in the following be designated "*monomict breccias*" and "*polymict breccias*" in analogy with the nomenclature often used for conglomerates containing only one kind of pebble or conglomerates containing several kinds of pebbles.

*The monomict brecciated stony meteorites* thus contain only material of one and the same kind, and seem in all cases known to the present author to have been formed by forces leading to a partial crushing of an earlier formed homogeneous stony meteorite. The monomict breccias belong principally to some group of achondrites other than the howardite group.

*The polymict brecciated stony meteorites* on the contrary contain fragments of different kinds embedded in a ground-mass, which in itself consists of small fragments of minerals of different kinds or of small fragments of minerals and of chondrules or fragments of chondrules and of glass. The polymict meteoritic breccias are thus principally accumulation breccias formed by debris and by chondrules of a great variety of different kinds. A certain amount of layering has also been observed (v. Reichenbach [2]) in some of these polymict brecciated stones.

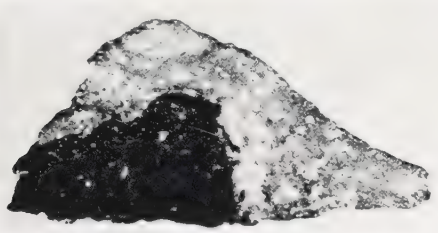

Fig. 3. Meteorite of "Hainaut." "Polymict breccia." Large fragments of "Black chondrite" and several small fragments of "White chondrite" in the "Grey chondrite." Natural size.

We have further to distinguish between brecciated stones of both the above kinds, which still appear as breccias in their original state as when formed and brecciated stones which, later on, during their cosmic development, have been subjected to strain, crushing and faulting, or to strong, often local heating or to several of these actions, whereby the original breccia structures have been more or less altered and even in part obliterated.

The unaltered breccias which have come to the knowledge of the author will here be dealt with first, the monomict breccias to begin with and the polymict breccias later. The description of some metamorphosed breccias will then follow.

### *Some examples of monomict brecciated stony meteorites*

Eucrites: Most of the eucrites have been crushed to a certain extent, after originally having been formed by crystallization of a magmatic mixture of molten silicates. They are therefore more or less brecciated, containing large irregular pieces of fairly even ophitic structure, cemented together by more crushed portions, which have often been reduced to mere mineral fragments, splinters and powder. Such portions of the eucrites thus represent typical "monomict breccias" produced by strain and crushing. *Jonzac* and *Juvinas* are probably the stones which contain the largest pieces and fragments of uncrushed material. They have also suffered less by heat action than have several of the other eucrites (Peramiho, Béréba). *Stannern* contains more crushed portions, but these seem to occur in different amounts in the various stones. This shows that the crushing of the ophitic stone had occurred already before it was broken up into the numerous small stones which fell at Stannern. Those stones which I have had the opportunity to see in several collections, do not seem to have suffered by heat.

I have not had an opportunity to examine the other eucrites. According to the description by BERWERTH [18] "*Peramiho*" has suffered a great deal both by crushing action and by strong local heating, resulting even in the formation of small black veinlets (formed by melting of the pyroxene or the bulk mass of the stone) and white veinlets (formed by local melting of the anorthite-bytownite).

"*Béréba*" is, according to the description by LACROIX [19], also a "monomict breccia," containing fragments of a coarse ophitic structure embedded in crushed portions of the rock. Portions of a more fine-grained, ophitic structure occur also and these LACROIX considers to have been formed secondarily by crystallization of local molten portions of the stone. LACROIX attributes the thermometamorphism of the original eucrite, of coarse ophitic structure, to several successive heatings of the stone.

"*Cachari*" seems, according to LACROIX [20], to have been subject to mechanical forces in a lesser degree than the other eucrites, no distinct brecciation structure having been developed. On the other hand it has been subject to a stronger local heating than any of the other eucrites mentioned here. In this case the heating has resulted in considerable quantities of the stone having melted and spread through cracks in the still unmolten portions, solidifying here to black veins.

"*Tscherony Koot*" is according to a picture published by KRINOW [21], a monomict breccia.

CHLADNITES: *Aubres* is a typical monomict breccia containing large fragments of clino-enstatite rock embedded in a mass of smaller fragments and splinters of clino-enstatite. Aubres contains neither diopside nor oldhamite and is therefore not a "Bustite" but a typical "Chladnite," although not so coarse grained and brittle as "*Bishopville*" and "*Khor Temiki.*"

DIOGENITES: "*Shalka*" is greatly crushed and consists of large and small fragments of hypersthene and hypersthene rock embedded in a small-grained mass of hypersthene fragments (TSCHERMAK [10] Pl. VI, Figure 1). Shalka, as well as "*Manegaon*" and "*Ibbenbühren*" (TSCHERMAK [10] Pl. VI, Figure 2) contains large uncrushed fragments and can thus be reckoned as belonging to the monomict breccias.

"*Johnstown*" [22] also is strongly crushed (comp. [22] Figure 3) and fragments of uncrushed material are embedded in the crushed debris (comp. [22] Figure 5); this diogenite may therefore be counted among the monomict breccias, to which also "*Tatahouine*" belongs on similar grounds, although, according to LACROIX [23], this remarkable stone has undergone at least two cosmic "thermometamorphisms."

The RODITE of "*Roda*," which according to the new analyses by RAOULT is chemically closely related to the diogenites, although like Johnstown containing a certain amount of plagioclase, is a "monomict breccia" consisting of large fragments embedded in a mixture of splinters and mineral fragments (WAHL).

Of the AMPHOTERITES at least "*Manbhoom*," "*Jelica*" and "*Vavilovka*" are monomict breccias.

"*Bandong*" contains portions of coarse and also of a finer grain but breccia-structures similar to those in monomict breccias have not been observed, although fragments of several kinds of chondrites occur in some sections (comp. p. 101).

"*Manbhoom*" is built up of large fragments of amphoterite embedded among small similar fragments and splinters of olivine and bronzite (WAHL).

"*Jelica*" is similar with regard to structure, but part of the fragments appear to be of a lighter colour than the ground-mass (Wahl).

"*Vavilovka*" is also similar, but here part of the ground-mass between the uncrushed larger fragments is lighter in colour than the fragments (Wahl).

Besides being a monomict breccia, Jelica also contains fragments of chondrites, lighter as well as darker than the ground-mass of the stone, and containing fairly large numbers of chondrules. In Vavilovka also fragments containing chondrules have been observed. The principal mass of these amphoterite thus form "monomict breccias," but since they contain also fragments of foreign material (chondrites of several kinds) they are, as a whole, "polymict breccias."

*Examples of "polymict breccias"*

(a) *Polymict breccias among the achondrites*

All the Howardites probably contain angular pieces of "eucrite" or of other kinds of achondrites embedded in the tuffaceous principal mass of mineral fragments of which this group of achondrites is built up; they are thus typical "polymict breccias."

"*Frankfort.*" The sample and microsections of Frankfort in the British Museum collection contain unaltered as well as remolten fragments of eucrite. Frankfort is thus a polymict breccia.

"*Garanhas.*" The samples of the howardite of Garanhas in the Paris collection contain fragments as well as a vein. Garanhas is therefore a veined howardite and a polymict breccia.

"*Le Telleul*" contains similar fragments. In the new description of this stone by Lacroix [19] he attributes the structure of the howardites (also of Luotolaks) entirely to the crushing of originally coarsely crystalline stones. However the presence of the angular fragments of various kinds is convincing proof that this view is not correct, but that the howardites are accumulation products, tuff breccias.

"*Luotolaks*" is a typical "Tuff-breccia" (Tschermak [10] Pl. IV, Figure 1 and 4) and contains numerous angular fragments of various kinds such as have earlier been briefly described by the author. Tschermak [10] reproduces a microphotograph of a eucrite fragment (Tschermak [10] Pl. IV, Figure 2). Other kinds of fragments are described later on (pp. 105–106).

"*Mässing.*" According to Tschermak this stone contains pieces of "eucrite" and of a dense or microcrystalline achondrite. However, no closer description of these fragments is given.

"*Pasamonte.*" According to the description by Foshag [23] and the pictures published by him and by Watson [17] (Figure 98, p. 189) Pasamonte is also a "polymict breccia."

"*Pavlovka.*" The sample in the Paris collection contains angular fragments of different kinds and Pavlovka is therefore a polymict breccia (comp. p. 107).

According to observations on the samples and sections in the British Museum "*Petersburg*" is a polymict breccia containing eucrite fragments.

"*Bolghati.*" This howardite differs somewhat from the other howardites in that the ground-mass is darker greyish black than the fragments of eucrite contained therein. It is a polymict breccia.

Bustite: "*Bustee.*" Like the *chladnites* the main portion of Bustee is principally built up of enstatite and clino-enstatite and is therefore closely related to the chladnites, but contains in addition certain amounts of a diopsidic, monoclinic pyroxene, small amounts of plagioclase (Tschermak [10] Pl. V, Figure 1 and 2), and of oldhamite. In this stone is embedded a large "nodule" or rounded fragment of a different kind of stone, consisting principally of the monoclinic, diopsidic pyroxene, mentioned above as a minor constituent of the principal portion of the stone, and of oldhamite together with small amounts of "osbornite." Bustee is considerably crushed and the principal portion has the character of a monomict breccia but together with the "nodule," contained therein it can be considered as a "polymict breccia."

Chladnites: "*Cumberland Falls,*" which has been referred to a special group, "Whitelyite," is in reality a typical "*Chladnite*" composed of enstatite and clino-enstatite but containing angular fairly large fragments of a "black chondrite" and small fragments and splinters of graphite. It is thus a typical polymict breccia, although the white principal mass is in itself a monomict breccia, as seen in the upper portion of Figure 1.

(b) *Polymict breccias among the chondrites*

Brecciation is much more common among the chondrites than among the achondrites, about 15% of the chondrites hitherto described having been classified as brecciated. The distribution of brecciated stones among the different classes of stones is, however, very unequal. The breccias seem to be most common among the "grey chondrites," 30% of these having been described as brecciated. Of the "spherical chondrites" 15% are given as brecciated, and of the "intermediate chondrites" 12%, of the "crystalline chondrites" also 12%, of the "white chondrites" 6%; but of the "black chondrites" and "crystalline spherical chondrites" none have so far been classified as brecciated. As far as the experience of the present author goes, all the brecciated chondrites are "polymict breccias," which is in good agreement with the—at least originally—tuffaceous character of all stones containing chondrules. All the "Howarditic chondrites" (to which small class 10 stones have been attributed) are typical polymict breccias*. There seems further to exist a strong predisposition for polymict breccias to develop into "grey chondrites."

In the following list those chondrites are given which have come to the notice of the present author as having been described as containing fragments of a different character from that of the main mass, or of which pictures have been published permitting them to be considered as "*polymict breccias:*"

*Assam*, Cg. v. Haidinger [24]. Dark pieces of a chondrite embedded in a lighter grey chondrite (sample in the Paris collection. Wahl).

* It seems, however, rather problematic whether this group of "howarditic chondrites," which was introduced by Brezina, should in future be upheld as a separate class of chondrites. The main characteristic of the group as given by Brezina was that just like the howardites the howarditic chondrites all contained enclosed angular fragments. If we examine the ten stones in question, we find that with regard to the principal mass of these stones they belong to several of the other classes of chondrites. They are thus only ten typical "polymict breccias" picked out among the stones belonging to other groups of chondrites, and differ largely among themselves with regard to their main mass.

*Borgo San Donnino*, Cho. Brezina.

*Bremervörde* (= Gnarrenburg), Cg. v. Reichenbach [2], St. Meunier [8].

*Canellas*, Ci. St. Meunier [25], Figure 61.

*Chandakapur*, Cw. contains according to v. Reichenbach [2] eucrite fragments.

*Chantonnay*, Cg. v. Reichenbach [2], Tschermak [10], [23], Cohen [12].

*Cullison*, Co. Merill [13] describes a large light-coloured nodular mass of "*Chladnite*," ten to 17 mm in size enclosed in the darker main mass (Pl. 55, Figures 1 and 2).

*Drake Creek* (= Nashville), Cw. Contains according to v. Reichenbach [2] grey fragments.

*Ensisheim*, Ck. v. Reichenbach [2] says "Ensisheim besteht aus zahlreichen vielgestaltigen, dunkelgrünen Brocken in eine hellere Grundmasse marmorartig eingebettet." Comp. also Cohen [11].

*Gerona*, Cc. Cohen [11].

*Gnadenfrei*, Cc. Lasault [27], Cohen [11].

*Harrison County*, Cho. Brezina.

*Homestead*, Cg. Lasault [27], Cohen [11].

*Knyahinya*, Cc. St. Meunier [25], Figures 63 and 64.

*Krähenberg*, Cho. Brezina.

*Lalitpur*, Cho. Brezina.

*Mangwendi*, Ci. Lightfoot, Macgregor and Golding [28] say: "The stone has a fragmental structure, with angular inclusions, either lighter or darker in colour than the matrix. One of these measures 4·5×4·5 cm but the majority are 1 cm or less."

*Mauritius*, Cho. Brezina.

*Mezo-Madaras*, Cc. St. Meunier [8].

*Monroe* (= Cabarras) Cg. St. Meunier [8].

*New Almelo*. Nininger [29].

*Orvinio*, Or. Tschermak [25].

*Ottawa*, Cho. Brezina.

*Oviedo* (= Elgueras = Cangas de Onis). Cohen [12].

*Parnallee*, Cg. Haidinger [4], Story Maskelyne [8], St. Meunier [8], [9], [25], Figures 65 and 66.

*Pulsora* (= Rutlam) Ci. Haidinger [6], Tschermak [10]. Three different kinds of fragments: white fragments, eucrite fragments and grey fragments.

*Santa Barbara*, Cho. Brezina.

*Sevilla*, Cho. Brezina.

*Siena* (= San Giovanni d'Asso), Cho. Brezina. St. Meunier [25], Figure 99.

*Shytal* (= Dacca), Ci. v. Haidinger [30], Tschermak [10], Cohen [11].

*Sitathali*, Cho. Brezina.

*Soko-Banja, Cc.* (= Sarbanovac). Tschermak [10], Cohen [11], St. Meunier [25], Figure 62.

*St. Mesmin*, Ci. St. Meunier [25], Figure 60, Tschermak [10], Cohen [11].

*Tysnaes* (= Midt Vaage), Cg. REUSCH [31].

*Waconda*, Cc. COHEN [11].

*Weston*, Cc. MERRILL [14] says: "The breccia-like structure is very evident, and is produced by angular pieces of a light grey colour embedded in the prevailing dark material. The chondrite structure is equally pronounced in both . . . ."

As we see from the above descriptions the "*monomict breccias*" *are all of secondary origin*, the brecciation having been caused by compression or crushing of a previously homogeneous stone. The "*polymict breccias*" on the contrary *are of primary origin*, having been formed by accumulation, like the volcanic tuff-breccias. In this case the peculiar brecciation has arisen from fragments of ready formed stony meteorites of different kinds having been embedded among the principal mass of these cosmic tuffs, containing mineral splinters and broken crystals, together with chondrules, pieces of chondrules, splinters of minerals and glass and mineral and glass powder and further nickel-iron and troilite grains, all accumulated together.

In Figures 4 and 6 microsections of some polymict stones are shown. Figure 6 shows an angular black fragment of "orvinite" in the stone from "Rush Creek" (p. 113) and Figure 4 a fragment of "rodite" (light portion) in the crystalline chondrite from "Plainview" (p. 111).

Some observations on polymict brecciated stones, together with petrographic descriptions of the fragments contained, will be given in the following part of this paper.

## OBSERVATIONS ON POLYMICT BRECCIATED STONY METEORITES AND FRAGMENTS CONTAINED THEREIN

A short description of those stones which have earlier been described, together with a reference to the principal petrographic description published, is given in the following with a view to facilitating comparisons between the character of the principal portion of the stone and the fragments it contains. The latter, which mostly represent so far undescribed portions of the meteorites, are described in more detail. Where the fragments represent types of meteorites which have been recorded in only a few cases but which form the principal mass of meteorites which have fallen or have been found, or which represent types of meteorites not known so far or described a more detailed description is given.

The meteorites and their fragments described here are listed in alphabetical order, irrespective of their position in the natural system of classification; use being made of the ROSE-TSCHERMAK system, without most of the extensions introduced by BREZINA. In a second smaller group those stones are dealt with which have undergone cosmic alterations after incorporation of the fragments.

*Akbarpur*, fell 18. 4. 1838, Cg. In one of the micro-sections belonging to the British Museum collection, a fragment—about 1 cm in size—of a spherical chondrite rich in chondrules was observed in the grey chondrite. Akbarpur is thus a polymict stone.

*Aleppo*, Syria, fell about 1873, Cwb. The thin-sections of this stone belonging to the Brezina collection of thin-sections of meteorites contain fragments of an achondrite of diogenitic composition but rich in felspar. The structure of these fragments reminds one of a "hornfels." The composition is that of a "*rodite*" rich in felspar.

*Arriba*. Lincoln Country, Colorado, found 1936, Ci. Macroscopically Arriba appears in some pieces to be rather strongly decomposed and rusty. It is medium iron-rich, most of the iron occurring in small particles, but quite a number of unevenly distributed grains up to 4 or 5 mm in size occur. Troilite is likewise unevenly distributed and occurs occasionally in still larger grains, often partly bordered by nickel-iron. The decomposition has affected the stone in an uneven manner, as a result of which considerable portions of the pieces or cut slabs show a dark brown colour on a surrounding light yellowish-grey background. These dark portions are very unevenly distributed and sometimes of rather large extent; dark portions up to 10–12 cm in size have been noticed by the author.

In micro-section the meteorite appears surprisingly little changed by this weathering, the dark portions merely appearing as more strongly impregnated by limonite than the lighter portions. The different zones of the crust were plainly seen in one section. The stone is rich in chondrules and has originally been an "intermediate" or a "grey" chondrite, which of these it is difficult to say with certainty on account of the present weathered condition, but probably it should be classified as an "intermediate chondrite, Ci."

The Arriba stone is not brecciated or veined, but in two micro-sections small angular pieces of quite different, achondritic character are visible. Arriba is thus as to origin a "polymict" accumulation product.

*Fragment a*. Looks very much like a very fine-grained apparently holocrystalline basic volcanic rock. Most of the individual mineral grains are too small to permit of a determination of their nature, but here and there, unevenly distributed, occur larger mineral grains and small clusters of such grains; these all consist of rhombic pyroxene. Between the grains of high refraction occur small interstitial areas of much lower refraction and double refraction, which presumably represent plagioclase or "maskelynite" grains. Judging from their higher double refraction a not inconsiderable number of the small mineral grains consists of olivine. Small opaque grains which appear to be chromite occur and also a few quite small particles with metallic reflection, probably troilite. This fragment, of which only a portion 3–4 mm in size is visible at the border of the section, can according to its mineral composition be designated as a piece of a fine-grained "*rodite*."

A most remarkable circumstance is that this achondrite fragment is traversed by a small "dyke" with sharp rectilinear borders. The dyke or vein is made up of a somewhat devitrified dark glass.

This fragment has thus undergone quite a complicated cosmic development before being enclosed among the chondritic particles on the formation, by accumulation, of the chondrite of Arriba. To begin with, it had crystallized as an igneous rock of which a considerable portion must have existed in order to allow it to be penetrated by a "dyke" of glassy magmatic material. The originally "volcanic," crystallized, igneous cosmic rock, similar in petrological composition to the meteoric stone which fell at Roda in Spain 1871, was, after having completely cooled, traversed by a dyke (or dykes) of magmatic material, which was rapidly chilled and solidified as a glassy dyke. After this the parent rock (fine-grained rodite) was at least in part crushed into small angular fragments, which were dispersed, some (or at least one) of them being admixed to the chondritic and fragmental material in process of accumulation to form the chondrule-rich chondrite of "Arriba."

*Fragment b* is also a fragment of a crystalline, igneous rock. It is holocrystalline, fine-grained, although of larger size of grain than fragment a. It consists only of rhombic pyroxene (bronzite or hypersthene) and a small quantity of chromite grains. It is thus a fragment of a "*diogenite*."

*Bandong*, Java, fell 10. 12. 1871, Amph. According to observations on the 2 kg stone in the Paris collection and eight good thin-sections, 3 in the Brezina collection, 4 in the Paris collection and 1 in the Helsingfors collection, the structure varies somewhat in different portions of the stone, some portions being of a larger size of grain than others. The stone contains comparatively much felspar and in some sections fragments of a foreign character occur:

(a) One section in the Brezina collection contains fragments which are richer in felspar than the main mass of the stone. In composition they correspond to a "*rodite*" and have probably been formed by crystallization from a silicate melt, but have later been altered by heat action, the felspar contained changing to "maskelynite."

(b) Fragments of black chondrites and a small fragment of "orvinite," not showing fluidal structure, in one of the sections of the Brezina collection, and a similar "orvinite" fragment in one of the Paris sections.

*Cangas de Onis*, Asturias, Spain, fell 6. 12. 1866, Cgb. The dark grey main mass of the 2 kg piece in the Paris collection contains fragments of a lighter colour.

*Chandakapur*, Berar, India, fell 6. 6. 1838, Ci. Both specimens of this stone in the British Museum collection contain a portion of a large fragment which is entirely different in character. Evidently the two specimens have originally been broken from one and the same of the three stones collected near Berar. The portion of the fragment contained in sample No. 16 868 is 6–7 cm in length and the original fragment, of which portions are now seen in the two samples in the British Museum, must have been of considerable size. The border line between the fragment and the surrounding main portion of Chandakapur is quite sharp. The main portion of Chandakapur is an "intermediate chondrite" of fairly even composition throughout. The fragment is in contrast studded with chondrules of various kinds and also with small angular fragments of different kinds: black, dense ones and light grey or greyish white ones being the most conspicious. This fragment is therefore in itself a "polymict breccia" of which a fragment was embedded in the Chandakapur stone when the latter was formed.

I am tempted to say that if the Chandakapur stone had been investigated and described at any time during the twenty years after it fell, the big fragmental piece in it could have been described as a kind of brecciated stony meteorite not known before. But in 1857 there fell two much larger stones, also in India, at Parnallee Madras. "*Parnallee*" has been described as a "brecciated grey chondrite" Cgb. Macroscopically investigated and on being compared, the fragment in Chandakapur and the 244 g piece and fragments No. 40876 of Parnallee in the British Museum collection, which have been broken from the large 60 kg stone, are found to be exactly alike. Had they not been labelled, the pieces 40876 could just as well have been broken from the fragment contained in the Chandakapur stone as from the Parnallee stone.

*Cumberland Falls*, Whitley, Co, Kentucky, "Whitleyite." Besides the large and small black fragments of a "black chondrite" of the "Farmington type," a small

light-coloured fragment of a quite microcrystalline, dense character has been observed. In thin section it shows angular, sharp borders towards the "monomict breccia" of large and small fragments of enstatite and of clino-enstatite, which build up the principal mass of the meteorite.

The fine grain prevents any optical determinations and it is therefore only possible to guess that the fragment is mainly a very fine-grained enstatite stone or a fine-grained diogenite of a kind not heretofore observed among the achondrites.

*Danville*, Morgan County. Alabama, U.S.A. fell 27. 11. 1868. Described as a veined grey chondrite. The small pieces in the collections at Helsingfors and in the British Museum look more like a "white chondrite." In the British Museum piece a fragment of grey chondrite is seen in the surrounding much lighter mass.

*Farmington*, Cs. Washington County, Kansas, fell 25. 6. 1890. One of the sections of this stone in the Helsingfors collection contains a fragment of an "amphoterite" of middle grain size measuring about three-quarters of a cm and also two smaller fragments of the same kind.

*Oubari*, Fezzan Sahara Orientale N.W. Africa, found 27. 9. 1944, Cg. When it was found by M. Lelubre this meteorite which is remarkable in many respects, was already broken up into a few large pieces (the largest about the size of a child's head) and a great number of small pieces and fragments which are now in the Musée d'Histoire Naturelle in Paris. Madame E. Jérémine is at present working out a detailed description of the stone, and she has had the kindness to show me the interesting material. Here I shall not give any details relating to the properties of the stone, but merely briefly mention some of the different kinds of fragments it contains, as these have a bearing on the problems regarding polymict brecciated meteorites discussed in this paper. For all general facts and details regarding the meteorite of Oubari, I should like to refer to the description of the meteorite which M. Jérémine will soon publish in this journal.

The surfaces of the stones, except where covered by the black crust, have in a peculiar way been polished by the desert wind and sand and appear quite glossy, with harder portions, such as chondrules, protruding over the greater part of the surface. The stone contains a great number of small and large black fragments, up to 2 cm in size, which show in a very conspicuous manner on the wind-polished glossy surfaces; also great numbers of light yellowish-brown and greenish-grey dense fragments are easily detected on these wind-polished surfaces. On a fresh surface it is, however, extremely difficult to distinguish these lighter fragments from the main mass of the stone and on such surfaces it is principally the often angular black fragments which show distinctly.

In my opinion, the stone of Oubari can be classified as a "*grey chondrite Cgb.*," since all the numerous fragments are contained in, or surrounded by material of this kind. Certain portions of this grey chondrite are fairly rich in chondrules of all the common kinds. There are, however, portions of the stone which contain more fragments than grey chondrite, and in some of the micro-sections it is difficult even to trace the grey chondrite at all. Conditions become more complicated because some of the fragments of lighter colour are built up of an intermediate chondrite, in thin-section not much differing from the principal mass of grey chondrite.

In thin-section the following kinds of fragments have so far been observed:

*Light fragments*

1. Pieces of medium- or fine-grained *amphoterite*. These fragments are the most abundant.

2. Pieces of an "*intermediate chondrite*." These chondrite fragments seem to contain somewhat less nickel-iron than is the case with the grey chondrite.

3. Madame JÉRÉMINE has studied in detail a fragment which is built up of large crystals of rhombic pyroxene with a "poikilitic" intergrowth of oligoclase. The rhombic pyroxene plates contain numerous small grains of olivine, which among themselves are not of similar orientation. Monocline pyroxene has also been observed by M. JÉRÉMINE in this peculiar rock fragment. I have never before seen any such large crystals of poikilitic structure in any stony meteorite. With regard to the structure, it resembles certain *grahamites*, but, in all cases I have studied, these contain more monoclinic pyroxene, and the plagioclase of the grahamites is an almost pure anorthite, whereas in this fragment it is an oligoclase, like the plagioclase of the enstatite-chondrites and other chondrites. This fragment must be regarded as the first specimen of its kind of a variety of basic rock not met with hitherto. Having regard to its appearance it could just as well be taken for a sample of a terrestrial rock as for a sample of a new kind of stony meteorite.

*Black fragments*

4. Fragments of "Orvinite."

5. Fragments of "Tadjerite."

6. Fragments of "black chondrite Cs" of the MCKINNEY type.

These numerous black fragments, of which many small ones are to be found in many of the larger thin sections, are of somewhat varying properties. We are entitled to say that, besides the above mentioned types 4, 5 and 6 a number of black fragments occur which according to their structure and properties stand between these three types of stony meteorites and, so to speak, form transitional types between these black stones already known for a long time. The study of the black fragments in "Oubari" and in other stones mentioned in this paper has also greatly contributed to form the opinion of the author that all the kinds of black chondrites so far known are closely related to one another. This is probably due to the circumstance that they all originate from several kinds of other meteorites by the same kind of process, by a "thermometamorphism," although this metamorphism has, in different cases, progressed to a different stage.

*Fleming*, Logan County, Colorado, found 1940, Cs. In the black chondrite, which belongs to the Vigarano-type of black chondrites, a large greyish black fragment—about half a cm in size—of a rather dense, fine-grained rock has been observed. In thin-section this fragment shows a very great resemblance to the non-fluidal dense portions of the stone from *Orvinio*, containing numerous small and somewhat larger fragments of olivine and rhomb. pyroxene in a black glass. This "Orvinite" fragment has thus been embedded in the stone simultaneously with the chondrules.

*Hainaut*, France (= "Lille" = "Bettrechies," Belgium) fell 26. 2. 1934, Cg. According to the monograph by LECOMPTE [32]. The stone consists of a rather firm cataclastic mass of a dark bluish-grey colour in which fragments of various colours and sizes are distributed.

The chondrules contained in the dark grey main mass are mostly white, but also grey chondrules occur. The chondrules are mostly about 2 mm in size and break with the surrounding mass.

*The fragments in the stone:* According to Figure 3. Plate I of the Memoire No. 66 [32], which is here reproduced as Figure 2; the white fragments are fairly abundant and mostly about 2 cm in size. There are six such white fragments to be seen in this picture. Just below the central white fragment, a small group of black fragments is seen. Lecompte mentions that the fragments vary from 7–30 mm in size and in one case a fragment 60 mm in size has been noticed. The white fragments are mostly rounded in shape.

According to Figure 3, reproduced here as Figure 3, and Figure 4 of Plate I of the Mémoire No. 69 [32], the black fragments are angular in shape, with sharp borders and attain a size of up to 3 cm.

According to my observations on pieces of the meteorite in the Musée d'Histoire Naturelle, Jardin des Plantes in Paris, the main mass of the stone should be classified as a *brecciated grey chondrite*, Cgb, and not as an intermediate chondrite Cib.

The light-coloured fragments contained in the principal mass are of at least two kinds:

(a) Fragments of a "white chondrite, Cw." These are both macroscopically and in thin-section entirely similar to "Mocs" and the numerous white chondrites of that type.

(b) Seen under the microscope some small fragments were found to be such of an "amphoterite" of medium grain.

The *black fragments* contained in the principal mass are in part macroscopically rather dense, black and brittle. These are in thin-section easily recognized as pieces of:

(c) "Orvinite," almost identical with those portions of the "Orvinio" stone consisting of small fragments of silicates embedded in a brownish black glass, which in Orvinio are surrounded by portions of fluidal appearence.

(d) A "black chondrite" of the "Farmington type." Most of the larger, angular black fragments seem to be of this kind.

In Memoire No. 66 [32]. Lecompte mentions:

(e) On page 13, "Dans les fragments de la brèche . . . par endroites de beaux groupements de cristaux allongées forment avec le pyroxène ou avec un verre, une belle texture ophitique."

(f) And on page 21: "Remnants of fragments of a poikilitic structure formed by plates of rhombic pyroxene in which rounded olivine portions are embedded."

The meteorite of "Hainaut" may thus be described as a "polymict" grey chondrite containing numerous fragments of a "white chondrite," of a "black chondrite of the Farmington type" and of "Orvinite," together with a few fragments of several kinds of "achondrites."

From a genetic point of view this stone is of considerable interest; it shows that while the "tuffitic" principal mass of the composition of a grey chondrite was being assembled—consisting of the usual components of such a chondrite: chondrules of various kinds, fragments of chondrules, fragments and dust of various minerals, principally rhombic pyroxenes and olivine, fragments and dust of glass, and grains and dust of troilite and nickel-iron, fragments of some white chondrite already existing—and thus formed at an earlier stage—together with fragments of similarly

earlier formed black chondrites and of Orvinite, were mixed with the other material and formed this polymict grey chondrite. And further it should be noted that the black chondrite fragments and the Orvinite fragments represent portions of stony meteorites, formed so much earlier that these meteorites had had time to be transformed into black chondrites and into Orvinites, these being themselves stones of a secondary origin, formed by a later heating up of other kinds of chondrites. All these meteorites had thus been formed, undergone a cosmic metamorphism and later been broken up into pieces, before their fragments took part in the formation of the stone of Hainaut.

*Hedjaz*, Arabia, fell 1910, Cg. The principal portion of the stone in the Paris collection is a typical "grey chondrite" which, however, contains a considerable number of fragments of other stones embedded in the grey chondrite. Macroscopically one observes black fragments of up to about $\frac{1}{2}$ cm in size and smaller yellowish-grey, dense fragments.

A few of these fragments are contained in the micro-sections studied. (a) A black fragment is an "*Orvinite*" piece very similar to the Orvinio sample in the Helsingfors collection, but resembles also certain orvinite-like portions of "Tadjera." (b) A light fragment contained in one of the micro-sections looks like a volcanic igneous rock and should most probably be classified as a "*Diogenite*" of fine grain.

*Leighton*, Colbert county, Alabama, U.S.A., fell 12. 1. 1907, Cgb. In the 96 g slice in the British Museum collection, angular pieces of "white chondrite" about one and a half and 2 cm in size, are to be seen.

*Le Telleul*, Manche, France, fell 14. 7. 1845, Ho. One of the micro-sections in the Helsingfors collection contains:

(a) A small fragment of a *Diogenite*, consisting of larger fragments of rhombic pyroxene embedded in a ground-mass of smaller and of very fine fragments and grains of the same mineral, together with some chromite grains.

(b) A small fragment of a *Chladnite* of middle grain size, consisting mostly of enstatite, together with a few somewhat larger grains of "clino-enstatite" (twinned).

(c) A micro-section prepared by the author from a dark grey fragment contained in the meteorite is a kind of a medium-grained pyroxenite consisting of about 70% hypersthene-augite and about 30% plagioclase, together with comparatively much chromite (and possibly some magnetite ?). The composition of this fragment is thus qualitatively that of a fine-grained eucrite, but the pyroxene is more abundant than in the ordinary eucrites.

(d) In an earlier publication I have described a small black fragment consisting of a portion of a crystal of rhombic pyroxene, which, however, was rendered quite dark owing to impregnation along cracks by an opaque black dust.

(e) Lacroix [19] has described fragments of *eucrite* and of remolten eucrite from the sample in the Paris collection.

*Luotolaks*, Savitaipale (Southern Savolaks), Finland, fell 13. 12. 1813, Ho. The black and grey fragments contained in the howardite of Luotolaks are very different in character, but most of them are probably eucrite fragments which have been more or less strongly altered by heat. We can thus distinguish between:

(a) practically unaltered eucrite fragments (Tschermak [10], Pl. IV, Figure 2), and

(b) fragments of recrystallized eucrite similar to those which Lacroix [19] has described from several howardites under the name of "fine-grained eucrite" and

which he has shown to originate from normal eucrite by recrystallization. As Lacroix has shown, such transformation of eucrite by heat can lead to very strongly altered products containing also quartz and magnetite in a glassy matrix.

(c) One of the black fragments in the howardite of Luotolaks, of which I have prepared a micro-section, contains large amounts of big anorthite fragments and of quartz fragments and some magnetite in a black glass, full of microlitic crystallizations. This fragment is in its turn traversed by a vein composed of a black glass of fluidal structure full of bubbles. Two different fragments were recognized as being of this same extraordinary veined type. These fragments are very similar to those containing quartz and felspar described by Lacroix in Luotolaks and some other howardites and in portions of some eucrites.

(d) A black fragment containing numerous anorthite laths (about three quarters of the whole mass) in a glassy mass full of small pyroxene fragments and remnants, together with chromite (?) grains.

(e) Dark grey fragments about $\frac{1}{2}$ cm in size. In thin-section it is seen to consist of large, slender prismatic and idiomorphic, optically nearly uniaxial monoclinic, pyroxenes embedded in a holocrystalline ground-mass of fine grain, consisting of grains of the same pyroxene, of plagioclase and troilite. This rock is very reminiscent of an augiteporphyrite with a holocrystalline ground-mass. Two fragments of this kind have been studied in thin-section. I have never seen any stony meteorite of this kind, but —in spite of its porphyritic character—it seems to me to be rather closely related to the meteoritic eucrites and howardites.

(f) Fragments consisting of enstatite grains. Two fragments of this kind, which can be classified as "*chladnites*" have been observed in a section.

(g) Just below the centre of the picture showing the tuff structure of Luotolaks published by Tschermak [10], Pl. IV, Figure 1, an angular piece, foreign to the surrounding mass, is seen. Tschermak refers to it as a "Gesteinbruchstück" and says in the description of the figure that it consists of a fine-grained mass of apparently mostly bronzite. This would thus be a fragment of a fine-grained "*Diogenite.*"

*Norcateur*, Decateur, Co, Kansas, found 1948, is an "intermediate" chondrite poor in chondrules, containing a network of dark veins which, at places where they branch, are fairly broad. These veins are almost entirely filled up with fragments of all sizes of olivines and rhomb. pyroxenes, of *amphoterite* pieces and, in lesser amount, pieces of chondrites. It seems evident that a dark, molten glass mass which was filled with these fragments has been forced into cracks in the stone.

In connection with the present investigation, it is of interest that in one of these brecciated veins a somewhat larger, sharply angular fragment of an entirely different material occurs. It is a fragment of a "*crystalline chondrite*" of rather fine grain, no chondrules being visible in this small portion. It contains, however, too large a quantity of metallic iron and sulphide grains to be classified as a fragment of an amphoterite, but it may possibly be regarded as belonging to some hitherto unknown group of "fine-grained crystalline chondrite" or of "fine-grained, crystalline achondrite," containing certain amounts of nickel-iron grains.

*Ochansk* (=Tabory), Perm, Russia, fell 30. 8. 1887, Cca. In a thin-section in the Helsingfors collection part of an angular fragment occurs. This fragment is fine-grained and looks like a piece of a microcrystalline, basic volcanic rock. It is so fine-grained that it is difficult to make any accurate measurements of the small

grains, but it seems that the bulk of the grains consists of olivine and bronzite, together with a fair amount of chromite and troilite grains scattered evenly over the section. This fragment seems thus to correspond to a very fine-grained "*amphoterite*," but I know of no amphoterite which is so fine-grained.

This fragment of fine-grained amphoterite is enveloped by a thin coating of metallic grains consisting principally of troilite, but with a small amount of nickel-iron. It seems as if these metallic constituents were in the molten state when they adhered to and covered the amphoterite fragment, afterwards crystallizing and forming a thin crust round the amphoterite fragment, the whole then being embedded in the tuffaceous mass of chondrules, fragments of chondrules and mineral fragments which make up the bulk of the "spherical chondrite" of Ochansk.

*Parnallee*, Madras, India, fell 28. 2. 1857. Two stones fell. The older investigations re the fragments contained in Parnallee have been mentioned on page 98. In spite of the stone being very rich in fragments it is rather difficult to obtain thin-sections of these without destroying much material. The big 60 kg piece (main mass of the larger stone) in the British Museum collection is almost entirely covered by crust and the stone is thus best studied from the smaller pieces, as these all seem to have been broken off from the lower portion of the big stone. I did not find any sections passing through a fragment, neither among the numerous old sections, some of great size, which have probably been prepared during the time of Story-Maskelyne, nor in recently prepared sections.

The 200 g Helsingfors stone, which probably originates from the smaller stone, and has been obtained through exchange from Henry Ward, is very similar to the Paris sample (from Lawrence Smith) and the sample No. 40876 in the British Museum. It shows on a polished surface, small light yellowish grey and also black fragments besides many mostly spherical chondrules. In the Helsingfors thin-sections a fragment of a *chladnite* of medium grain measuring about $\frac{1}{2}$ cm and two similar small fragments have been studied. A fragment of *Orvinite* is included in the sections in the collection in Paris.

Besides fragments of minerals Stanislas Meunier mentions fragments of *white chondrite* ("Luceite"), of *chladnite*, of *chassignite*, of *tadjerite* and of three kinds of "rock types" so far unknown among the investigated meteorites up to that time.

*Pawlowka*, Saratov, Russia, fell 2. 8. 1882, Ho. Besides fragments of eucrite and of what he considers as molten and recrystallized fragments of eucrites, Lacroix describes some fragments of peculiar character:

(a) "On trouve, en outre, de gros fragments grenus formés de pyroxène et d'anorthite, ayant la structure granulitique de la beerbachite." Lacroix doubts whether these fragments represent a rock possessing its original structure of crystallization or whether it is a recrystallization product. As mentioned above, the present author has observed rather similar fragments in Luotolaks and le Telleul. Since these fragments at least in part are sharply angular and are now embedded in a mass consisting of splinters and debris of pyroxenes and anorthite—which mass (main mass of the howardite) shows no signs of having suffered heating or melting—it is evident that should the fragments in question no longer have their original structure, they must have acquired their present structure before the fragments were split off from some larger piece and embedded in the present howarditic mass.

(b) " . . . un gros débris de pyroxène renfermant une plage de quartz bordé de magnetite."

(c) "De petits fragments constitués par de menus grains de quartz, associés à du pyroxène et à de la magnétite.

*Pulsora* (= "Rutlam" = "Ratlam State"), Ratlam State, Central India, fell 16. 3. 1863, Cib. v. Haidinger describes angular pieces of up to half an inch in size embedded in the somewhat darker ash-grey main mass of the meteorite. In the sample in the Paris collection fragments of lighter colour occur in the grey main mass. Also the sample in the British Museum collection No. 43059 contains a fairly large fragment of what is probably a "*white chondrite*" embedded in the grey main mass of the stone.

*Shelbourne*, Grey County, Ontario, Canada, fell 13. 8. 1904, Cga. According to the description of Borgström [34]. Shelbourne is a grey chondrite. One of the micro-sections in the Helsingfors collection contains a portion of a fragment, measuring 1 cm, of a peculiar kind of volcanic rock. This rock consists of fairly large, mostly idiomorphic rhombic pyroxenes evenly distributed in a kind of ground-mass made up of pyroxene laths, of much lower double refraction than the porphyric rhombic pyroxenes. These laths are embedded in a dark, greyish-brown glass, which fills only the angles left between the rather closely packed laths. In spite of their long lathformed shape these pyroxenes of the ground-mass have rather indistinct border lines and show between crossed nicols a polysynthetic twinning, which is, however, not so regular as for instance in the plagioclases and more like the twinning of the clino-enstatites in chondrules of various chondrites, but of greater width and irregularity. On account of the smallness and confused structure of the laths it is difficult to make exact optical determinations, but it seems certain that we have here to deal with a monoclinic pyroxene, probably a member of the clino-enstatite group (clino-bronzite ?). The glass is in places quite clear and translucent but mostly it shows signs of beginning devitrification. Its colour indicates that it is iron-rich. Thus we here have to do with a fragment of a basic magnesium-iron-rich "porphyric volcanic rock" of "diogenitic composition," hitherto not known among the stony meteorites.

*Soko-Banja* (= "Sarbanovac"), Aleksinac, Serbia, Cc., fell 13. 10. 1877. The large piece in the Paris collection (1·8 kg) contains fragments 1½ 2 cm in size, which in part are light grey and dense, and in part dark.

One of the micro-sections in the Helsingfors collection contains a portion of a fragment of "*Diogenite*" of small grain size. This fragment measures at least ½ cm and apparently consists almost entirely of rhombic pyroxene with a few larger fragments of the same mineral. Small opaque grains also contained in this rock seem to be principally troilite and chromite, with only some single grain of nickel-iron. This fragment probably corresponds to the dense, light-grey fragments of the Paris stone.

Tschermak ([10] p. 170) mentions in *Soko-Banja* angular fragments of up to 15 cm length consisting of a dark chondrite, which shows signs of having been strongly heated.

*Tulia*, Swisher County, Texas, found 1924. One of the micro-sections of this stone I have had the opportunity to study contains an angular black fragment, which under the microscope is quite similar to those portions of *Orvinio* which are not fluidal. This fragment can thus be classified as an "*Orvinite*."

*Polymict brecciated chondrites, which have undergone metamorphic alterations during their cosmic history*

In the preceding chapter a description has been given of polymict brecciated chondrites which apparently have not undergone any extensive alteration since they were formed. We know, however, of a large number of chondrites which do not contain any foreign fragments and are not brecciated in the same way as the stones described above, but which have been altered and metamorphosed after they were formed. In certain cases the stones have, evidently during their cosmic period, been cracked and molten material thereupon injected in cracks. This has solidified in the cracks, forming "veins" which in some cases are quite thin, in others broad, and often branching and spreading into finer veins. Such stones are generally not spoken of as "brecciated" but as "veined stony meteorites." We also know a certain number of stones, originally not brecciated, the "black chondrites" (about two dozen), which, after they were formed as various kinds of stony meteorites, have been blackened by heat effects, the heating up having occurred at one or more times during their cosmic evolution.

But there are also among the "crystalline chondrites" stones which the present author is able to interpret only as having originally been "polymict breccias" of various kinds though containing great numbers of fragments, which later on during their cosmic evolution have been subjected to a prolonged heat action, sufficiently strong to allow of a recrystallization and "welding" together of the fragments and the portions between the fragments and therefore in certain cases to allow a more or less far-reaching amount of obliteration of the distinct border lines of the fragments. Some of these stones look on the surfaces of polished slabs like dark, mottled gneisses and could easily be mistaken for such, were they not studded full of particles of metallic iron, Figure 5. In some respects they resemble marbles, their structures especially resembling those of dark marbles; and probably it is stony meteorites of this kind which PARTSCH, TSCHERMAK and COHEN have had in mind when speaking of "marble structure" in brecciated stony meteorites. I have not seen sufficiently large samples of the stones mentioned by the said authors, and such structures can be distinctly seen only on fairly large polished surfaces or cut slabs, while the fragments, and what one could describe as "ghosts" of fragments, are often only seen distinctly in reflected light at certain angles.

A stone of this kind, found at "*Plainview*," Texas, has been described by MERRILL in several short papers [16], and later on Dr. H. H. NININGER has managed to trace a great number of stones of this find, more than 900 of a total weight of about 700 kg, in an area sixteen miles long by four miles wide*. Other stones of this group are the large "*Hugoton*," Kansas stone and the "*Rush Creek*," Colorado stone, of which the main masses are all in the Nininger Collection. Dr. NININGER has kindly placed some samples of these stones at the disposal of the author for investigation purposes. But since the stones are of a rather complicated structure, only the main points of interest with regard to the contents of fragments of a different character from that of the main mass are dealt with here.

* The Nininger collection of Meteorites, A Catalog. Winslow, Arizona, 1950 pp. 13, 14. 83–87, 116a. Pl. XXIX, Figure 15 and 18, Pl. XXX, Figure 1, Pl. XXXIV ("Plainview I"). For "Plainview II" comp. p. 132.

*Plainview*, Hale County, Texas, found 1917, Cckb. This stone has sometimes been described as a "veined intermediate chondrite." Merrill [16] says in his first paper on this meteorite: "I have classed it provisionally as a spherical chondrite (Cc.)". In an addendum to the first paper and in his second paper Merrill points out that the stone is brecciated, consisting of about equal parts of light grey and darker grey more or less angular areas. He further says that both portions are chondritic, but that the dark portions show more distinctly spherical chondrules. In this paper he suggests "that the stone is a true breccia composed of fragments of a spherical chondrite and a veined intermediate chondrite." Merrill, however, emphasizes that even on polished surfaces it is not easy to recognize the different fragments of the breccia, although in certain cases, especially in reflected light, the border lines of the dark fragments are quite distinct.

In most respects I can corroborate Dr. Merrills brief descriptions of this very complicated stone. I have also met with the same difficulties as Merrill in making observations on the fragments and their structure, but already in this connection I should like to add a few comments, although a more thorough description must be reserved for a special publication.

I have investigated several small polished slices, and thin-sections from them, which show no brecciation but are fairly homogeneous. The stones are fairly hard, dark and rich in evenly distributed nickel-iron grains. I think Merrill is utterly wrong in classifying such a stone as an "intermediate chondrite." According to the specimens I have seen, it is a typical "*crystalline spherical chondrite*, Cck." The analysis by Whitfield, published by Merrill, is in important respects also quite misleading. Whitfield gives 6·22 % metallic nickel-iron and 9·57 % troilite, that is about one and a half times the amount of troilite as compared with nickel-iron. As easily seen from the polished slabs, there is on the contrary at least twice as much nickel-iron as troilite and the nickel-iron content is at least two and a half times that given by Whitfield.

As mentioned, Merrill describes fragments of a light grey chondrite and of a darker grey chondrite. In some slices I have observed such light fragments which often are distinctly angular. They are pieces of a light grey chondrite, which are embedded in a dark grey chondrite of the "Chantonnay" type, here and there exhibiting small portions with more or less distinct "black veins" ("Plainview I").

Other pieces ("Plainview II") contain dark fragments with quite distinct boundaries, and in thin-section these reveal themselves as fragments of "black chondrites" of the "Farmington type," which sometimes have distinct borders, and sometimes seem as if welded together with the lighter coloured Cck. material between the fragments. This melting together of fragments and surrounding mass explains the often "ghostlike" remants of the fragments, as seen on some of the polished surfaces.

The light yellowish white fragments shown on Plate XXXIV of the Nininger catalogue are lighter and of a much more dense character than the fragments of light grey chondrite mentioned above; they show in thin-section quite sharp boundaries towards the surrounding "crystalline spherical chondrite." They consist of an even-grained "*Rodite*," which is of finer grain than the Roda stone, from which it also differs structurally by the olivine occurring in small round grains scattered in the

fairly large individuals of rhombic pyroxene which are often poikilitically intergrown with plagioclase, the latter occurring in smaller quantity than the olivine (Figure 4).

From what is seen in those pieces of this stone of rather complicated character, which I, so far, have investigated, I should say that it has originally been a grey chondrite containing comparatively few and small chondrules, but on the other hand in certain portions large amounts of fragments of a light grey chondrite ("Plainview I") and in other portions fragments of a black chondrite of the Farmington type ("Plainview II"), measuring from one to 2 cm in size. This chondrite has, during its cosmic history, been heated, probably at many different times, and to varying degrees in different portions of the stone or stones. This has resulted in a "thermometamorphism" leading to a "crystalline spherical chondrite" or in some parts to a "crystalline chondrite" in which the original angular fragments of a light grey or of a black chondrite can still be observed in certain portions, although more or less recrystallized; in other portions there are only "ghost"-like remains of them, and in still further portions these remains can hardly be traced and the stone here appears as a fairly homogeneous "crystalline spherical chondrite" or as a "crystalline chondrite."

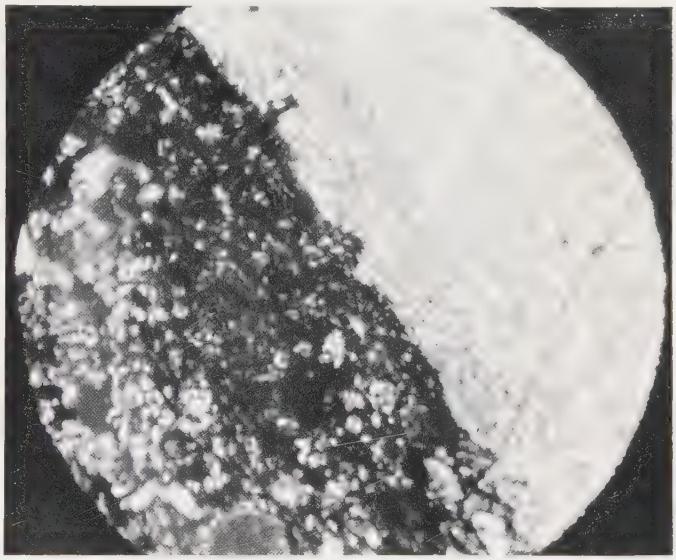

Fig. 4. Meteorite of "Plainview." Fragment of "Rodite" (light, right half of picture) in "Crystalline chondrite of Plainview" (dark, left) Micro section enlarg. 16×.

*Rush Creek*, Kiowa Country, Colorado, found in 1938. This is a stone which during its cosmic evolution has perhaps undergone still greater metamorphism than Plainview.

Seen on a polished slab one could easily take this stone for a dark "gneiss" with interstitial portions of lighter material, if there were not so many small grains of nickel-iron often together with much larger grains of troilite plainly visible. Figure 5 is a photo of a polished slab. The stone shows a certain amount of layering, but has, after its formation, been subject to mechanical forces resulting in a development of "slickenside" surfaces, and afterwards a certain amount of crushing has taken place in one direction. Further, the stone is somewhat cracked, and these cracks are filled, with secondarily depsoited limonite, which also to a certain extent impregnates the whole stone and probably makes it look altogether darker than it would otherwise appear, and also in thin-section appears as a yellowish brown impregnation of the sections.

In thin-section the meteorite in certain sections at first sight appears to be an "achondrite." But on closer inspection some chondrules, or what could be more exactly described as altered chondrules, remains of various kinds of chondrules, and "ghosts" of chondrules are found. In some sections no veins are seen, but in others there appear strongly branched veins consisting of a glass dark in parts, but in other portions much lighter. In some sections the stone is seen to contain many large and small fragments of "*amphoteritic*" or of "*diogenitic*" composition and also black

Fig. 5. Meteorite of "Rush Creek," polished slab. $\frac{3}{4}$ natural size. "Polymict breccia" showing "marble structure."

fragments (Fig. 6) of which all, so far seen in the thin-sections, are "*orvinites.*" In other sections the occurrence of the light-coloured fragments is obscured by the crushing of the stone which has taken place after its formation. There are small portions in the stone which could be described as amphoterites and others which could be described as diogenites or rodites if there were not such considerable amounts of metallic constituents distributed over the whole mass of the stone and the remains of chondrules here and there in the otherwise amphoteritic portions.

It is not possible to give here a detailed description of this, apparently, from what has been said, evidently very inhomogeneous meteorite. Judging from the material I have so far had the opportunity to investigate, I should say that the stone has originally been an intermediate or grey chondrite, containing large numbers of fragments of an amphoteritic character, like the stones of "Douar M'guila" and of "Oubari." Later on, during its cosmic evolution, it has become heated at one or more times, as a result of which portions have been entirely molten and the molten mass spread in cracks in the stone, solidifying in the cold portions as glassy veins.

Other portions of the stone have been less strongly exposed to radiation and heating, but anyhow sufficiently so as to have been partly recrystallized, the chondrules being much altered and recrystallized, and the "intermediate chondrite" changing to a more crystalline condition, greatly resembling an igneous rock, only the remains of chondrules in some portions showing that this structure is of a secondary character. Also, the amphoteritic and diogenitic fragments contained in the chondrite have been partly recrystallized during this period. Still later on, a certain amount of crushing and the formation of "slickenside" surfaces has taken place.

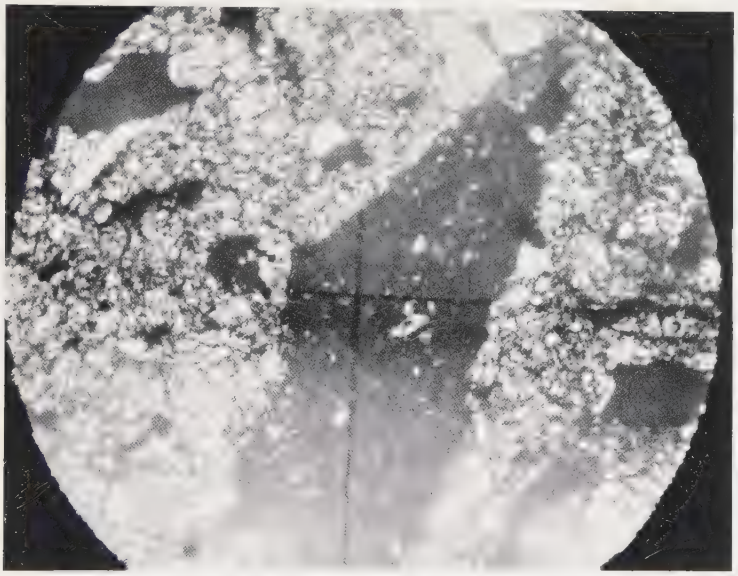

Fig. 6. Meteorite of "Rush Creek" micro-section. 70×.
Black fragment of "Orvinite" in "Crystalline chondrite."

*Hugoton*, Stevens County, Kansas, Ckb., found 1935. The large stone of Hugoton also seems originally to have been a chondrite rich in fragments of a black chondrite. This chondrite seems to have been metamorphosed later on by heat action and recrystallized, being thus altered to a "crystalline chondrite." So far the stone seems not to have been cut and the material of the outer portions is too strongly weathered and limonitized to permit of a more detailed investigation. It is, however, possible to see from thin-sections that the fragments have been pieces of a "*black chondrite.*"

## Summary

The above investigations on the brecciated *polymict stony meteorites* show that the fragments they contain are of the following kinds (Table 1).

*Table 1*

I. Fragments of Achondrites

1. *Chladnites*, in *Le Teilleul*, Ho. *Luotolaks*, Ho. *Parnallee*, Cg. *Cullison*, Cc. (Merrill.)
2. *Diogenites*, in *Arriba*, Ci. *Hedjaz*, Cg. *Shelbourne*, Cga. *Soko-Banja*, Cc.
3. *Rodites*, in *Arriba*, Ci. *Plainview*, Cck.

4. *Amphoterites*, in *Douar M'guilia*, Ci. *Oubari*, Cg. *Hainaut*, Cg. *Farmington*, Cs.
5. *Eucrites*, in all *Howardites* so far investigated.

II. Fragments of Chondrites

6. *White Chondrites*, in *Pulsora*, Ci. *Hainaut*, Cg. *Leighton*, Cg.
7. *Intermediate Chondrites*, in *Oubari*, Cg.
8. *Grey Chondrites*, in *Danville*, Cg.
9. *Orvinites*, in *Bandong*, Am. *Oubari*, Cg. *Hainaut*, Cg. *Hedjaz*, Cg. *Parnallee*, Cg. *Fleming*, Cs. *Tulia*, Cck. *Rush Creek*, Ck.
10. *Tadjerites*, in *Oubari*, Cg.
11. *Black Chondrites*, in *Cumberland Falls*, Chl. *Bandong*, Am. *Oubari*, Cg. *Hainaut*, Cg. *Plainview*, Cck. *Hugoton*, Ck.
12. *Spherical Chondrites*, in *Akbarpur*, Cg.

III. Fragments of Hitherto Unknown Kinds of Stony Meteorites

In *Cumberland Falls* (fragments of fine-grained chladnitic or diogenitic rock), in *Bandong* (fragment of roditic rock), in *Aleppo* (fragment of roditic rock), in *Oubari* (fragment 3), in *Hainaut* (fragments e and f) in *Hedjaz* (fragment b of fine-grained diogenitic rock), in *Luotolaks* (fragments c and e), in *Norcateur* (fragment of crystalline rock containing nickel-iron grains), in *Ochansk* (fragment of fine-grained amphoteritic rock), in *Parnallee* (according to Stanislas Meunier fragments of three different kinds of unknown rock).

The different kinds of stony meteorites contain the following kinds of fragments (Table 2).

*Table 2*

Achondrites

1. *Chladnites* contain fragments of: *Diogenites, Black Chondrites.*
2. *Diogenites*—
3. *Rodites*—
4. *Amphoterites*, contain fragments of: Various kinds of *Chondrites.*
5. *Eucrites*—
6. *Howardites*, contain fragments of: *Eucrites, remolten Eucrites, Chladnites* and of some unknown kinds of meteorites.

Chondrites

1. *White Chondrites* (Only one stone as yet investigated.) *Rodite* fragment.
2. *Intermediate Chondrites*, contain fragments of: *Diogenites, Rodites, Amphoterites, White Chondrites.*
3. *Grey Chondrites*, contain fragments of: *Chladnites, Diogenites, Amphoterites, White Chondrites, Intermediate Chondrites, Orvinites, Tadjerites, Black Chondrites, Spherical Chondrites.*
4. *Black Chondrites*, contain fragments of: *Amphoterites, Orvinites.*
5. *Spherical Chondrites*, contain fragments of: *Chladnites, Amphoterites, Black Chondrites.*
6. *Crystalline spherical Chondrites*, contain fragments of: *Rodites, Amphoterites, Orvinites, Black Chondrites.*
7. *Crystalline Chondrites*, contain fragments of: *Orvinites, Black Chondrites.*

Only results obtained by a personal study of thin-sections of fragments have been tabulated in Tables 1 and 2. As seen from Table 1 and the detailed descriptions on pp. 99–113, twenty-six stony meteorites have been studied with regard to the fragments contained. Besides this, the earlier, mostly macroscopic observations by different authors on thirty-seven stony meteorites have been abstracted and are referred to on pp. 97–99, but these older results have not been incorporated in Tables 1 and 2 since the observations on the fragments do not give any accurate

information as regards the kinds of meteorites to which the fragments belong. Further the results regarding sixteen "monomict breccias" have been given on pp. 94–96. At present we thus have a certain amount of comparative knowledge regarding seventy-nine of the rather more than a hundred stony meteorites which have been mentioned as being "brecciated."

The investigation of the fragments of stones foreign to the surrounding kind of meteorite was begun a long time ago in connection with the investigation of the pyroxenes of meteorites [12], and a few fragments not belonging to any kind of then known classes of stony meteorites were mentioned in the said publication. Observations at that period were made principally on the 800 sections of the Brezina collection since there were very few thin-sections of stony meteorites in the Helsingfors collection—less than half-a-dozen—with the exception of those from stones fallen in Finland, of which numerous sections had been prepared. It is only in recent years that sections of a great number of the stones of this collection have been prepared, and it is principally this material which has rendered it possible to carry out part of the present investigation. But the greater part of the stone samples in this collection are too small to allow of a study of the brecciation on a sufficient scale, and part of the research work has been possible only through the obliging kindness of the Director of the Mineral department of the *British Museum of Natural History*, Lt.-Col., Dr. Campbell Smith and the Director of the Mineral department of the *Musée d'Histoire Naturelle, Jardin des Plantes*, Dr. J. Orcel, in permitting me to study the large collections and the great numbers of thin-sections of these museums during visits to London and Paris during the last few years. I am also much indebted to Dr. M. H. Hey, of the *British Museum* and Mme E. Jérémine of the *Mineralogical Laboratory, Jardin des Plantes*, for kind help.

It is of great importance that this investigation should be continued and if possible extended to the stones mentioned on pp. 97–99 and to other brecciated stony meteorites and siderolites. The author therefore takes the liberty of appealing to the Directors and Staffs of Museums possessing meteorite collections, with a request for information with regard to brecciated stones containing conspicuous angular fragments and to the occurrence in the collections of their museum of any thin-sections, which happen to contain such fragments. The investigation of cases where a fragment is of sufficient size to allow of both the preparation of thin-sections and the making of an analysis—as in the so far unique case of *Cumberland Falls*—would be of special interest.

## General Conclusions

As seen from Table 1, nearly all kinds of achondrites occur among the fragments contained in other meteorites. The case is similar to that of the chondrites, of which all kinds, with the exception of the crystalline chondrites (Cck., Ck. and Cek.) occur as fragments.

Table 2 shows which of the several different kinds of stony meteorites have so far been observed as carrying fragments of other meteorites. Of the achondrites only some Chladnites, the Bustite, some of the Amphoterites and probably all Howardites have as yet been found to carry fragments of other kinds of meteorites. As regards the few white chondrites which have been described as brecciated,

I have had the opportunity to examine only one specimen containing fragments. All other kinds of chondrites are represented in Table 2. As seen from this Table most kinds of chondrites carry fragments of achondrites (chladnites, diogenites, rodites, amphoterites) as well as other kinds of chondrites. The grey chondrites have been found to carry a great number of different kinds (ten, out of a total of twelve) different kinds of fragments, which is, however, not surprising, seeing that brecciated stones are more numerous among the grey chondrites than among any other kind of stony meteorites.

We find thus, *that representatives of nearly every special kind of stony meteorite so far known carry fragments of most kinds of other stony meteorites*, and from this remarkable result of the present investigation we may now with a fair amount of probability conclude, that:

1. *At the time when the various kinds of polymict stones were formed there already existed at the same place in space fragments of most kinds of meteorites which have been observed to fall on the earth, and in addition a number of kinds of meteorites of which we have not yet any known separate fall.*

2. *All the various kinds of stony meteorites must have had their origin on the same cosmic body or on cosmic bodies of exactly similar composition, since they contain fragments of nearly all other kinds of meteorites.*

3. The polymict chondrites containing fragments of other kinds of stony meteorites are necessarily by origin accumulation products ("tuffs").

4. Only those achondrites which are not brecciated and contain no fragments of a foreign character and the "monomict breccias" among the achondrites can be of igneous magmatic origin, formed by crystallization. Examples of such crystallization product, crystallized magmas, in origin are thus reduced to the Eucrites, some Chladnites, Diogenites, Rodites, some of the Amphoterites, the Chassignite, the Angrite and the Nakhlite.

5. A study of Tables 1 and 2 shows that individuals of most kinds of stony meteorites have been formed at very different periods of time, since some individuals contain fragments of stones of a kind, individuals of which in their turn contain fragments of the first kind of stone. Thus, for instance, certain amphoterites contain fragments of grey chondrites and certain grey chondrites contain fragments of amphoterites.

6. Since some of the fragments in polymict brecciated stony meteorites, like those of "Black chondrites," "Tadjerites" and "Orvinites," are themselves stones which originally have been formed as various other kinds of chondrites, but which during their cosmic history have later, by heat action, been metamorphosed into Black Chondrites or Tadjerites or Orvinites, and then still later on broken into fragments, the formation of primary accumulation stones, like the spherical chondrites, must have taken place on one and the same cosmic body from which all the different kinds of stony meteorites originate (according to 2). The formation of all these kinds of stones must have taken place during a considerable period of time to allow all the secondary characters visible, for instance, in the veined grey and the black chondrites to have been developed by cosmic metamorphic processes, and for fragments of these stones then in their turn to have been enclosed in spherical chondrites and other kinds of unmetamorphosed stony meteorites.

7. The occurrence of fragments of kinds still unknown as stony meteorites (Table 1, III. Fragments) shows that we may expect that in future still further kinds of meteorites than those known at present will be collected or seen to fall.

Should recent observations by some astronomers, by which it has been possible to calculate the orbits of some newly fallen stony meteorites [35] (*Tilden*, 13. 7. 1927, Ci., *Paragould* [36], 17. 2. 1930, Cg., *Archie*, 10. 8. 1931, g.), be in future shown to be of sufficient accuracy, and in other cases be further confirmed, at least some white and some grey chondrites have belonged to cosmic bodies moving in orbits similar to those of certain of the *asteroids* which approach the orbit of the earth (Hermes, Apollo, Adonis for example), and we may further conclude:

8. That the stony meteorites originate from a body, or bodies, of asteroidal character (*cf.* 1 and 2) and that these in their turn originate from some, at one time single body, which at least in part consisted of material of the kind we know from the meteorites collected on the earth.

The investigation of the fragments contained in "polymict stony meteorites" thus throws some light on the important cosmic problems of the origin and cosmic evolution of the meteorites, and perhaps also on that of the asteroids.

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# The geochemistry of thallium

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ABSTRACT

A new analytical method has been developed for the determination of thallium in silicates. Numerous analyses of minerals and rocks have been made, to establish the distribution and mode of occurrence of thallium, especially in the common rocks. A double-arc spectrochemical method was used, giving a precision of $\pm 20\%$ and a sensitivity limit close to 0·05 ppm thallium.

Thallium occurs in igneous minerals and rocks by substitution for potassium. Its geochemical behaviour closely resembles rubidium, so that it is concentrated in residual magmas to occur in notable amounts in pegmatitic potassium minerals. It is also concentrated in certain sulphides. During erosion thallium goes into true solution as the univalent cation, but is removed from solution by adsorption in clays. Under strong oxidising conditions it accumulates in manganiferous deposits; a strong reducing environment also concentrates thallium to a slight degree in carbonaceous shales.

A new figure of 1·3 ppm is calculated for the crustal abundance of thallium, and the geochemical balance is discussed. Rubidium-thallium ratios for various materials are computed, and their significance discussed. Some aspects of thallium geochemistry are shown to be relevant to fundamental questions of petrogenesis.

## Introduction

"The tasks of geochemistry are firstly to determine the composition of the earth, and secondly to find the laws of distribution of the elements." This rather free translation from Goldschmidt [15] indicates the scope of the science whose foundations he laid. During the following ten years the distribution and abundance of most of the elements were studied by Goldschmidt and his associates, and the main outlines of geochemistry had been filled in.

Several elements however still remain comparatively little known, and one such element is thallium. It is clear that thallium is a very rare element, and lack of knowledge of its distribution has been due to difficulties in its estimation. Recent advances in spectrochemical techniques however have produced some pertinent results. Ahrens [5] made a study of thallium in pegmatitic minerals, and his very interesting results were reviewed by Rankama [47].

To determine thallium in rocks and minerals it was first necessary to develop suitable methods of analysis. These are described in the first section (see also Shaw, Joensuu and Ahrens [59]). In the second part the geochemical results are discussed.

The work described in this paper has been presented as a doctoral dissertation in the University of Chicago.

## Analytical Methods

### *Previous methods*

There are numerous standardised methods for the determination of thallium in all branches of analytical chemistry. A bibliography is given by Waggaman, Heffner and Gee [65]. Detailed consideration of the wide variety of methods is, however, outside the scope of this paper. Mention will be made only of the methods which are relevant to geological materials.

Hartley and Ramage [23] made some of the earliest spectrochemical studies of minor element distribution in minerals. Iron ores and other ores were analysed qualitatively by excitation in the oxy-hydrogen flame. Thallium was detected in a number of samples.

Vernadsky [64] established the presence of thallium in micas and feldspars by a combined chemical and spectrographic method.

Zies [67] carried out some of the first analyses of silicate rocks for thallium. Rock samples were decomposed by hydrofluoric and sulphuric acids in the usual manner for rock analysis, and the heavy trace elements precipitated in two groups of sulphides (copper-tin and zinc groups). Thallium was precipitated in the copper-tin group. The sulphides were examined by the rather elementary spectrographic techniques then in use. However, considerable care was taken and the results were informative.

In two important papers I. and W. Noddack [38], [39] investigated the abundance and distribution of the elements (including thallium) in the earth and meteorites. Unfortunately, no details of their analytical methods were given beyond the statement that chemical, spectrographic and X-ray spectrographic techniques were used.

V. M. Goldschmidt and his associates in Göttingen and Oslo, from 1929–1936, carried out numerous determinations of the abundances of minor elements. The cathode-layer spectrographic method (Mannkopff and Peters [32]) was used for determinations of thallium in rocks and minerals, this work being performed by Goldschmidt and Hormann. Results up to this date are given by Goldschmidt [18].

Some estimations of thallium in rocks were made by Van Tongeren [63]. The conventional cathode-layer spectrographic technique was used.

A series of papers from the Hamburg Institute from 1935 onwards gave details of new experimental techniques for determining minute quantities of the heavy volatile elements. By heating powdered beryl in vacuum to a high temperature in a silica-glass tube R. Böse obtained sublimates of the volatile metals on the cooler portions of the tube (Rose and Böse [50]; Böse [8]). The sublimates were oxidised, then removed by solution and redeposited in the borings of graphite electrodes. By arcing the electrodes elements such as Ga, Ag, Ge, Cs, Zn were identified, whilst ordinary spectrographic analyses of the minerals seldom revealed their presence. These methods were developed further by Preuss and Ottemann.

Preuss [45] utilised the volatility of thallium to determine the minute traces present in normal rocks and minerals. Samples of up to 3 g of finely powdered rocks were heated in a carbon electric furnace in a gentle current of inert gas which carried the liberated gases into a carbon arc through a hollow graphite cathode. In that way the volatile heavy metals were fractionally-distilled, giving considerably greater sensitivity than was previously possible, in spite of a difficult and slow instrumental technique. The metals studied included Cd, Hg, In, Tl, Ge, Sb and Bi, and sensitivity of the order of 0·03 ppm was obtained for thallium; no internal standard was used.

Ottemann [43] also used an auxiliary furnace for studies on the volatile elements, in a manner similar to that of Böse. The distillation was carried out in a vacuum line, so that gases such as $CO_2$, $H_2O$ and $F_2$ could be studied directly by spark discharge. The volatilised metals were collected as a sublimate on the furnace tube, from which they were dissolved in acid. The solution was transferred to the boring in a graphite electrode and evaporated. The residue was then arced by the usual cathode layer methods, and the photographic plates compared visually with standard plates made in the same manner. A sensitivity limit of 0·001–0·005 ppm was thus obtained, using initially a sample of at least 3 g.

Further work was carried out by Rusanov and his associates (Rusanov [51]; Rusanov and Alekseeva [52]) on the determination of thallium and other elements in minerals, using a flame source for spectroscopic analysis. With sphalerite for example the powdered mineral was spread on a cigarette paper saturated with ammonium sulphate and burned in an oxy-acetylene flame. In qualitative analyses the presence of 5 ppm thallium could be detected, and in quantitative analyses (using cobalt as internal standard) thallium could be measured in the concentration range 10 to 300 ppm with an accuracy estimated at $\pm 13\%$.

Stoiber [60] analysed a large number of sphalerite samples for several trace-elements including thallium. His method was a straightforward spectrographic technique using the D.C. arc. Results were obtained by visual comparison with standard plates, and were therefore semi-quantitative, but of considerable interest.

Oftedal [42] studied the accessory elements in a large number of sulphides from Norwegian zinc-blende deposits. Thallium was determined in a similar manner to the other elements, *i.e.* by mixing the powdered sulphides with graphite and analysing by the usual spectrographic methods. The cathode-layer method was used and also the alternative procedure where the spectrograph slit is evenly illuminated. It should be mentioned that Oftedal found no increased sensitivity in the cathode-layer for thallium ("Die Thalliumlinien sind von dem Glimmschicht-effekt wenig beeinflußt:" Oftedal [42], p. 19). The sensitivity limit was about 10 ppm.

A very similar problem was investigated by Strock [62], who also studied the determination of trace elements in zinc sulphides. The sulphides were mixed with graphite powder and with a buffer of NaCl carrying beryllium as internal standard. Sensitivity for thallium was only 100 ppm and no experimental results are quoted.

Ahrens has published several papers on thallium in silicate rocks and minerals (Ahrens [1], [2], [3], [4], [5]; Ahrens and Liebenberg [6]). A description of this method is given in the first paper. Samples of alkali silicates and clays were arced in graphite electrodes, using anode excitation. The advantages of this method are that background interference is minimised and fractional distillation is enhanced. Greater sensitivity is thereby obtained, and Ahrens reported that 0·3 ppm of $Tl_2O$ could be measured: no internal standard was used.

Scribner and Mullin [57] described a very interesting spectrographic method for determination of impurities in uranium. Utilising the high volatility of many heavy metals, these could be fractionally distilled into the arc, using a carrier agent of intermediate volatility, with anode excitation. 2% of gallium oxide was mixed with each sample, to act as carrier agent and sweep out the volatile impurities whilst it evaporated. Samples of 100 mg were arced in special graphite electrodes. The method had previously been used by Hasler [25] with ammonium chloride as a carrier, and although neither method has been tried with geological materials they appeared very promising. A sensitivity of only 3 ppm was obtained by Scribner and Mullin for thallium, but they did not use either of the two strongest spectral lines.

Marks and Potter [34] have investigated the analysis of ores, flue dusts and similar enriched samples for thallium, by means of a straightforward spectrographic arcing procedure. The "total-energy method" of complete combustion of an accurately weighed sample was utilised, and the effects of extraneous elements considered. Control analyses by chemical methods demonstrated that only fair precision was attained. It seems probable that considerably better accuracy could have been reached, had an internal standard been used. Comparison of the rates of volatilisation of thallium and tin (Marks and Hall [33]) at the same arc-current indicates that tin would be suitable as internal standard if arc temperatures are stabilised *e.g.* by addition of abundant alkali to the samples, and if an exposure time of at least 50 sec is used.

### *Analysis method*

A spectrochemical analytical method was used, and details of the equipment are to be found in the tabulation at the conclusion of this section.

In recent years several new arcing procedures have been developed for specific analytical problems, involving the use of special electrodes or chemical compounds. Some have been mentioned in the preceding section (*e.g.* Hasler [25]; Scribner and Mullin [57]), and were investigated to see whether a suitable method could be developed. The essential criterion was high sensitivity, and it was not found possible to achieve a sensitivity greater than about 0·5 ppm by these methods.

To determine the minute thallium concentrations in most rocks a highly sensitive method was necessary. A double-arc procedure was suggested by L. H. Ahrens, and experiment showed that this technique was satisfactory (Shaw, Joensuu and Ahrens [59]).

The double-arc method uses the principle of fractional distillation mentioned earlier. A relatively large sample of the rock powder and flux is placed in a graphite crucible which is held by an auxiliary stand between the arc electrodes (see Fig. 1 and 2). Initially the furnace or crucible is in contact with both electrodes. When the current is switched on and the electrodes moved away from the furnace, two separate arcs will be struck, one between the lower electrode and the base of the furnace, and the other between the furnace-cap and the upper electrode. The lower arc heats the furnace and sample, while the upper arc serves for excitation of the materials distilled from the sample. By suitable adjustment of the operating current and exposure

time, the line intensities of the readily volatile elements are enhanced with respect to more refractory elements, thereby greatly increasing the sensitivity for these volatile elements.

Many factors influence the excitation conditions and only a few have been adequately studied, such as the design of the electrodes and the choice of flux or buffer. Furnace electrodes and caps were machined from 3/8 in., 1/2 in., 3/4 in. and 1 in. diameter graphite rod. A wide, short furnace is much preferable to a narrow long one, since the powder is less likely to be blown out by sudden gas expansion. Moreover with a wide and shallow furnace the heating of the sample is more regular.

During the initial arcing period, the sample is heating and is emitting little vapour. To suppress the intense CN bands formed at this time, the furnace cap and the upper electrode were impregnated with a concentrated aqueous solution of the flux used (usually lithium carbonate), by rapid drying on a hot plate. Alternatively the arc could be screened for the first 5 sec of each exposure. (A screening for 2 sec was in fact always carried out.)

The polarity of the lower electrode was negative, and the upper one was positive, so that the base of the furnace acts as anode, and the cap as the cathode. This establishes a heat gradient from bottom to top, assisting the evaporation. By focussing the arc on the slit, it was shown that a cathode-layer enrichment (Mannkopff and Peters [32]) takes place as with the ordinary arc.

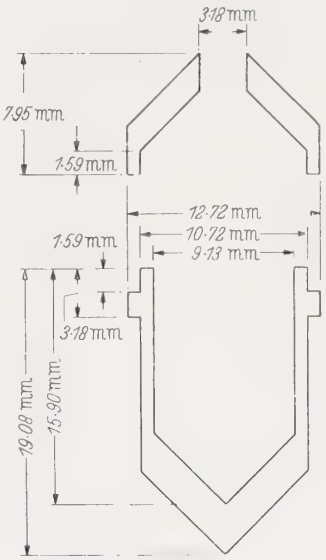


Fig. 1.
Double-arc furnace electrode.

An alkali salt was mixed with the sample, as a fluxing agent. The abundance of alkali metal vapours helps to lower the temperature of the arc and stabilise it, to facilitate the excitation of elements of similar ionisation potential, and also to suppress CN band spectra. It was found that thallium behaves most suitably when three parts of the rock are mixed with one of sodium or lithium carbonate.

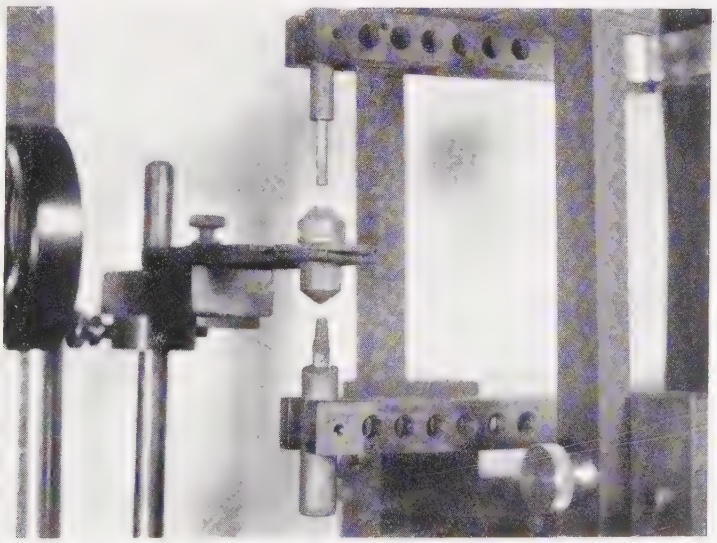

Fig. 2. Double-arc electrode assembly.

Also, bearing in mind the success of the "carrier-distillation" methods used by Scribner and Mullin [57] and Hasler [25], the use of carriers such as ammonium chloride, gallium

oxide, silver chloride and oxalic acid was tested. Ammonium chloride was found to give the best enhancement of the thallium line, and sensitivity similar to that obtained when using an alkali flux.

Using an alkali salt as flux, the band spectra were cut down to a very low level and so the more sensitive type 103 plates could be used. The same low band-spectrum level was obtained also with the use of a carrier agent. The arc burn is, however, rather unstable when using a carrier at a fairly low current ($5\frac{1}{2}$ amp) and so a mixture of three parts lithium carbonate, one part ammonium chloride and twelve parts rock powder was investigated and found the most suitable of all. The total sample was usually 560 mg, in a furnace of dimensions shown in Fig. 1. With low-density materials such as kaolin and loess, however, a sample of 400 mg was used.

It is necessary now to consider the behaviour of the arcs during the burning of a sample, as certain aspects of the technique differ considerably from the ordinary D.C. methods.

During the initial stage both arcs are quite unstable, for little vapour is being emitted by the sample, and the current is carried by the relatively large resistance of the furnace and cap *. The usual procedure, therefore (with a current of 7 amp), was to strike the lower arc alone for 2 sec, then to strike the upper arc, which was screened for a further 2 sec. By then the furnace had become incandescent and the sample was partially melted. For the first 10 sec, both arcs wander considerably, and burn very noisily, the current fluctuating between 5 and 8 amp. During this period either arc is likely to extinguish, and the other must follow suit. With practice, however, interruptions of this kind can be largely prevented. After the initial 10 sec the burning becomes more quiet and steady, and the current is stabilised, as abundant buffer and sample are being distilled into the upper arc. This persists for 90 to 120 sec, when the burning becomes irregular again, and the blue light of the arc indicates the presence of CN bands, the flux and much of the sample having been evaporated.

By increasing the current say to 10 amp the initial burning is much more steady but the band spectra and continuous background are increased too much. On the other hand, a lower current, whilst decreasing the background density, gives too great instability in the burning.

The effect of arcing the alkali salts such as halite, ocean residues etc., is naturally to buffer the arc to a very low temperature; melting occurs almost at once, and the molten mass frequently bubbles out from the furnace cap. The alkali spectra are very intense, and usually a large amount of continuous background is obtained. Under these conditions it was found better to use the less sensitive 111-D plates instead of the 103-F type.

It was decided early in the work to attempt to measure other elements of high volatility as well as thallium. The results of Preuss [45] and others suggested that the rates of volatilisation of metals such as In, Pb, Bi, Ga, Sn, Zn, and Rb, were similar. Moving plate exposures with these elements were made, indicating that In, Bi, Pb and Sn appear to be completely volatilised from samples under the exposure and current conditions suitable for thallium, but the others are too involatile. Tin was later chosen as internal standard, but analyses were carried out for indium, lead, bismuth and thallium.

## *Analytical procedures*

In the photographic process the type 103-F and 103-O plates were used because of their high sensitivity. At first they were developed as directed by the manufacturers, but the high fog-level on the 103-F type plate (Density S = 0·34) would lead to a loss of sensitivity which could not be tolerated. By cutting the development time from 4 min to 3 min, the fog density was very much decreased without appreciable loss of density of the spectral analysis lines. Considerable sensitivity increase was thus obtained.

Rocks and minerals were first crushed in a steel mortar, then ground in an agate mortar by a *Fisher* Automatic Grinder, with the usual precautions as to sampling and avoidance of contamination. The whole of the initial sample was crushed until it passed through 150 mesh silk bolting-cloth, then dried at 105° C and kept in a desiccator.

The mixture of lithium carbonate, ammonium chloride and the internal standard was prepared by sieving through a new 100 mesh brass sieve until homogeneous. The precise

* The cap to the furnace must be tight-fitting to make good electrical contact.

composition of the flux was of no great importance provided that any new batch was calibrated against the old by making control exposures with standards.

Tin was used as the internal standard, as mentioned previously, because of its close similarity in behaviour with thallium in the arc and the suitability of its spectral lines. Blank arcings were made with no sample in the furnace electrode to make sure no thallium or tin were present as contamination in the graphite, and the purity of the flux salts was then checked by blank exposure, giving satisfactory results.

Two spectral lines were chosen for analysis purposes. The first, (Thallium A) was the most sensitive line Tl 5350·46 Å * and this was used for the lower concentrations. For higher concentrations, the line Tl 2921·52 Å was used (Thallium B). The former was photographed on plate type 103-F and the latter on plate type 103-O. These thallium lines permitted the measurement of a range in concentration from 0·05 ppm to 1000 ppm. The corresponding internal standard lines were chosen to be as close as possible to these lines, to avoid variations in plate sensitivity, to be of suitable intensity for photometric measurement, and to be free from possible coincidences. The lines selected were Sn 4524·741 Å and Sn 3032·775 Å. There is a coincidence of a weak titanium line, Ti 4524·732 Å, with the former, but this was negligible except in materials very rich in titanium, such as ilmenite.

For reliable results in spectrographic analysis it is essential that the standard mixtures should resemble closely the materials to be analysed, both in bulk chemical composition and in the nature of the individual components. Variations in the matrix of the standards have been shown to give considerable changes in intensity of the analysis line (Marks and Potter [34]). Also the state of chemical combination of the analysis element in the standards is important: *e.g.* if the element is incorporated in the standard mixtures as an oxide, these standards might not be very suitable for comparison with samples where the element is in a silicate. Obviously it is impossible to achieve satisfaction in these matters where a wide variety of samples is to be analysed, and so compromises have to be made.

It was fortunate that a silicate glass containing a known amount of thallium metal (11·98 % Tl) was available. This glass, prepared by the Research Department of the *Leeds and Northrup Company*, was eminently suitable as a standard for measuring thallium in silicates.

Three materials were chosen for standard matrix. The first was a pure silica-glass fused under vacuum and kindly supplied by Dr. I. Friedman. The other two were specimens of bytownite and dunite. All three were carefully checked and found free of thallium and tin. Also each was separately arced with a known (low) concentration of thallium under identical conditions. In this way, it was shown that the densities of the recorded lines were almost identical and thus there was little variation in excitation due to variation in contents of $SiO_2$, MgO, CaO, and $Al_2O_3$. For the standard matrix equal parts by weight of each of these (crushed to pass a 200 mesh silk screen) were mixed by repeated sieving.

The first standard contained 0·1 % Tl. The thallium glass and matrix were weighed, then homogenised in an agate mortar. Successive standards were made by dilution in the usual way in steps of 1:0·316 down to 0·000032 % or 0·32 parts per million (ppm).

The analytical procedure is summarised in Table 1.

### *Photometry and calculations*

A great deal has been written on the problems of evaluating accurate analyses from photometric data (*e.g.* Strock [61]; Mitchell [36]; Kaiser [28]; *et al*). It is not necessary to discuss this here, as various standard procedures have been evolved for different types of problems.

For each exposure a six-step spectrum was obtained. The step-sector was rotated at a speed sufficient to overcome the possibility of reciprocity failure, in view of the relatively long exposure time (90 sec). For plate calibration all six steps of one of the analysis or internal standard lines were used, whenever possible. Since analyses were also being carried out for indium and lead it was usually possible to choose the best of three or four lines on each plate for calibration, judging them from the standpoints of the amount of background and the possibilities of self-reversal. It was previously confirmed, of course, that the plate calibration curves would be the same in each case, *i.e.* that the plate sensitivity-wave length curves were reasonably constant.

* All wavelengths have been taken from the M.I.T. Standard Wavelength Tables (Harrison [22]).

*Table 1. Arcing procedure for thallium with the double-arc method*

| | |
|---|---|
| Spectrograph | 21 ft grating instrument by *Jarrell-Ash Company* with Wadsworth type mounting: dispersion 5 Å/mm in first order spectrum |
| Power source | Emitator by *Bolidens-Gruv AB*, Sweden |
| Voltage | 225 v D.C. |
| Current | 7 amp |
| Electrodes | Anode (Upper), 1/8 in. diameter graphite rod (*National Carbon Company*, "Special" Grade)<br>Cathode (Lower), 3/16 in. diameter graphite rod (*National Carbon Company*, "Special" Grade)<br>Furnace, dimensions as in Fig. 1 (*National Carbon Company*, "Regular" grade) |
| Arc gaps | Upper 9 mm<br>Lower 2 mm |
| Slit | Length 12 mm; width 30 μ |
| Step-sector | Seven-step sector by *Jarrell-Ash Company*: step ratio 1:2 |
| Optical system | Arc focussed on a diaphragm by a short-focus spherical lens. Its image focussed on the spectrograph mirror by a long-focus cylindrical lens placed just in front of the slit |
| Exposure | 90 sec |
| Plates | *Eastman-Kodak* Compan No. 103-F and 103-O |
| Developing | Plate 103-F—3 min at 20° C in *Eastman-Kodak* Developer D-19<br>Plate 103-O—4 min at 20° C in *Eastman-Kodak* Developer D-19 |
| Sample | One part of flux (1 $NH_4Cl$ + 3 $Li_2CO_3$ + internal standard) homogenised in an agate mortar with three parts of the rock sample, previously dried at 105° C. Total weight of sample usually 560 mg, containing 0·5 % $SnO_2$ |
| Spectrum lines | Tl 5350·46 Å (designated Tl "A")<br>Tl 2921·52 Å (designated Tl "B"<br>Sn 4524·741 Å<br>Sn 3032·775 Å |
| Photometer | *Leeds and Northrup* Recording Photo-Densitometer |

In plotting the plate calibration curve, a calculation board was employed. Measurements on the photo-densitometer gave figures expressing the densities of the lines ($S$-values)*.

Thus

$$S = \log \frac{A_0}{A}$$

where $A$ is the intensity of light transmitted by the image of the line and $A_0$ is the intensity of light transmitted by an unexposed part of the plate.

The ordinate scale of the calculating-board converted these $S$ values by the Seidel transformation (Honerjäger-Sohm and Kaiser [27]), into $W$ values, where

$$W = \log\left(\frac{A_0}{A} + 1\right).$$

These $W$-values were plotted against the logarithm of the relative exposure time for the successive steps in the spectral line.

Wherever possible, the background and three steps of each analysis line were measured. and the background and one step of the internal standard line. Background corrections were

* The nomenclature of Kaiser [28] is used throughout this paper.

applied in the usual way, and the ratio of the intensity of the analysis line $I_z$ to the intensity of the internal standard line $I_s$ measured on the abscissa as $dY_{z,s}$ where

$$dY_{z,s} = \log \frac{I_z}{I_s} = \log I_z - \log I_s .$$

To construct the standard curves, three sets of standards were exposed. This gave three exposures for each point, but one or two had to be discarded due to poor arcing conditions. The upper limit of concentration for the thallium "A" line was about 15 ppm, whilst the lower limit for thallium "B" was a little lower (by extrapolation). Thus an adequate coverage for the whole concentration scale was obtained.

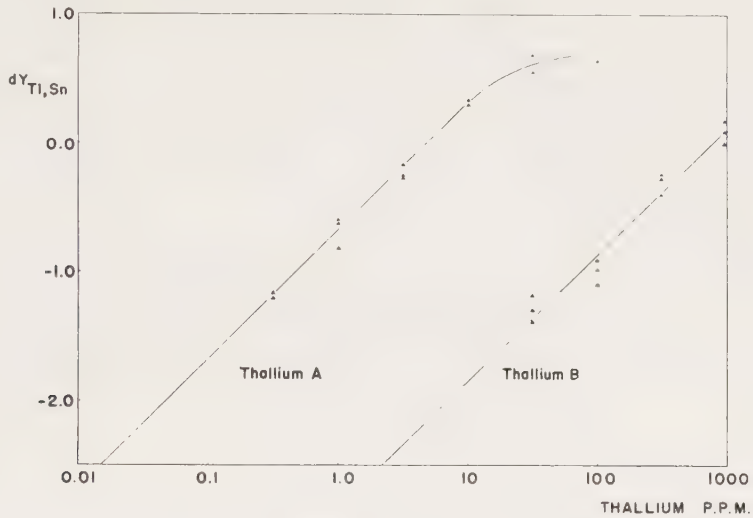


Fig. 3. Standard curves for thallium.

In plotting the curves (reproduced in Fig. 3) the $dY_{z,s}$ values were plotted as ordinates and the logarithm of concentration as abscissa.

Due to the lack of stability in the arc burn, and the frequent tendency for some of the sample to be blown out of the furnace electrode or for the molten sample to bubble out of the furnace cap, the distribution of the points around the curves was not entirely satisfactory, and a fairly large reproductibility error was present. Nevertheless Fig. 3 shows that: (a) the deviation from the curves is no greater at low than at high concentration, and (b) there is no suggestion for a tail to develop at the lower ends of the curves, which would indicate thallium present in the matrix of the standards. Therefore, it was felt quite possible to extrapolate the "A" curve to a low concentration limit.

The R.M.S. deviation of the points around the standard curves was $\pm 30\,\%$. It was decided to run analyses in duplicate, thus decreasing the standard error by a factor of $1/\sqrt{2}$ to about 20 %, which seemed satisfactory for the present purpose. As mentioned above, analyses were being carried out also for certain other elements, and inspection of the standard curves prepared for lead, indium and bismuth confirmed an impression already obtained, namely that the size of the R.M.S. deviation was due mostly to occasional wide fluctuations from the curve, and the majority of deviations were less.

The chief aim in the development of this new arcing technique was to increase the analytical sensitivity. It is seen from the standard curves that extrapolation beyond the lowest step is quite permissible, but it is difficult to decide what figure to take as a sensitivity limit. The problem is to determine the smallest density difference between a line and its background which can be measured with any accuracy. KAISER [29] has explored this question with his customary thoroughness, but the results are applicable only to analyses of considerable precision. It was therefore decided to take the empirical relation used by HASLER and KEMP [26] as a useful

working-figure. They take the sensitivity-limit as the concentration for which the analysis line has an intensity of 0·3 times the background level. Using this relationship it was found that the sensitivity limit lies in the range 0·02–0·10 ppm. This rather wide range exists because the sensitivity depends on the background to a small extent, but also on the intensity of the internal standard line, which is influenced by the nature of the sample.

An average figure for the sensitivity limit would be 0·05 ppm, with an error of ± 20 %. This is sufficient for the present purpose, permitting the estimation of thallium in most silicate materials and the outlining of the main features of its geochemistry.

The foregoing remarks on sensitivity and error apply of course exclusively to the silicate rocks. It is also necessary to judge the results from samples of other kinds.

The use of an internal standard in spectrochemical analysis, is of course to compensate for the variations in excitation conditions due to samples of different nature and due to fluctuations in the arc. But an internal standard is not reliable under all conditions, and is of value only in environments where it behaves with close similarity to the analysis element. In some samples (*e.g.* those rich in manganese and iron, and the ocean salts) the tin lines were plainly suppressed to a considerable degree, and it is not possible to estimate whether such a suppression has also taken place with thallium in the absence of independent analyses. However, in a personal communication to Dr. Kalervo Rankama, Professor T. Watanabé of Osaka University in Japan, confirmed the suppression of thallium lines by iron.

It was decided therefore to calculate the thallium content for meteorites, sulphides, oxides, carbonates and salts in the usual manner, but the possible unreliability of the results should be borne in mind. The number of analyses, in any case, in each of these important groups is insufficient to give any average figures or show important trends. It is particularly regretted that time did not permit a full and accurate series of sulphide analyses to be made, in view of the economic significance of these minerals in the geochemistry of thallium.

## The Geochemistry of Thallium

### *Results of the analyses*

Table 2 contains the results of analyses for thallium in minerals and rocks, expressed in parts per million (*i.e.* grams per metric ton) to two significant figures. The second figure is always retained, even when it indicates thousandths of one part per million, since the concentration scale is expressed in logarithmic units. However, although this procedure is theoretically correct, the second figure is probably much less reliable at low concentrations.

The symbol "tr." indicates that the thallium line was present but too weak measure; wherever possible the sensitivity limit is also indicated. The symbol "—" indicates that the thallium line was not visible.

The content of thallium in some rocks and minerals was estimated to be so extremely low that one may ask whether these figures have any significance, or whether they might represent contamination by extraneous materials. The latter is not believed to be the case, as all samples were handled in exactly the same way, and extreme care was taken to avoid possible contamination. Moreover, the fact that in many samples no thallium at all could be detected would bear out this conclusion. The figures representing tenths and hundredths of 1 ppm are believed to be of the same order of accuracy as higher values.

Some analyses appear more than once in the table, since certain materials fall in two of the groups; thus an analysis of quartz is listed both with oxides and with tektosilicates.

It will be recalled that each figure represents the mean of two analyses, and is believed to have an accuracy of +20 %.

*Table 2. Analyses of rocks and minerals for thallium*

| *Sample Number* | *Sample* | *Locality* | Tl *ppm* |
|---|---|---|---|
| | | MINERALS | |
| | | *Native elements* | |
| S 69 | Graphite | Kärpälä, Mäntyharju, Finland | 0·49 |
| S 152 | Graphite | Blackdonald Mine, Renfrew Co., Ontario | — |
| | | *Oxides and hydrated oxides* | |
| S 99 | Quartz | Custer Mt., Black Hills, S. Dakota | — |
| S 129 | Opal | Grand Manan Is., New Brunswick, Canada | 0·043 |
| S 116 | Magnetite | Seabrook Lake, Mississagi Reserve, Ont. (extracted from Lamprophyre S 12) | 0·36 |
| S 20 | Hematite | Pöpönsaari, Suojärvi, K.F.S.S.R. | — |
| S 19 | Limonite | Haapakylä, Evijärvi, Finland | tr. <0·06 |
| S 154 | Iron oxides | Säppi, Luvia, Finland (extracted from Diabase S 138) | 0·023 |
| S 170 | Pyrolusite | (not known) about | 1·0* |
| | | *Sulphides* | |
| S 173 | Pyrite | Crystal Falls, Michigan (see Slate S 174) | tr. <0·05 |
| S 131 | Pyrrhotite | Creighton Mine, Sudbury, Ontario | 0·074 |
| S 134 | Chalcopyrite | Creighton Mine, Sudbury, Ontario | 0·028 |
| S 135 | Sphalerite | Beck Mine, Pitkäranta, K.F.S.S.R. | tr. <0·006 |
| S 132 | Marcasite | Veules, Normandy | 0·24 |
| S 136 | Galena | Säkkijärvi, Finland | 0·27 |
| S 133 | Molybdenite | Temagami, Ontario | 0·008 |
| | | *Halides* | |
| S 127 | Fluorite | Cardiff Tp., Ontario | —** |
| S 4 | Halite | Grand Saline Salt Dome, Texas | — |
| S 3 | Sylvinite rock | near Carlsbad, New Mexico | — |
| | | *Phosphate* | |
| S 101 | Apatite | Custer Mt., Black Hills, S. Dakota | 0·23 |
| | | *Silicates* | |
| | | a) Nesosilicates | |
| S 139 | Olivine rock | S. Massif, Khabozero, Kola Peninsula U.S.S.R. | 0·11 |
| S 180 | Olivine rock | (not known) | — |
| S 165 | Almandine | Koirinkoski, Kitilä, K.F.S.S.R. | 0·007 |
| S 42 | Garnet | Adirondacks, N.Y. | 0·019 |
| S 46b | Garnet | N. Stromfjord, Greenland | 0·009 |
| S 167 | Epidote | (not known) | tr. |
| S 168 | Staurolite | (not known) | — |
| S 128 | Zircon | Mt. Titanium, Georgia, U.S.A. | 0·36 |
| S 123 | Titanite | Eganville, Renfrew Co., Ontario | 0·15 |
| | | b) Inosilicates | |
| S 47 | Hypersthene | Rifkol, W. Greenland | tr. |
| S 11 | Hypersthene | Stillwater Complex, Montana | — |
| S 124 | Diopside | Ojamo, Lohja, Finland | tr. |

* Estimated by visual comparison.

** The thallium line was hidden by an intense CaF band spectrum.

*Table 2. (Continued)*

| *Sample Number* | *Sample* | *Locality* | Tl *ppm* |
|---|---|---|---|
| S 115 | Augite | Seabrook Lake, Mississagi Reserve, Ontario (separated from Lamprophyre S 12) | 0·044 |
| S 122 | Tremolite | Lee, Massachusetts | 0·65 |
| S 169 | Hornblende | (not known) | 0·31 |
| | | c) Phyllosilicates | |
| S 94 | Muscovite | Kuutelokallio, Kaatiala, Kuortane, Finland | 16·0 |
| S 102 | Muscovite | Custer Mt., Black Hills, S. Dakota | 47·0 |
| S 95 | Phlogopite | Skräbböle, Parainen, Finland | 78·0 |
| S 175 | Biotite | (not known) | 11·0 |
| S 96 | Lepidolite | Custer Mt., Black Hills, S. Dakota | 95·0 |
| S 172 | Chlorite | (not known) | -- |
| S 18 | Kaolin | Werran Hills, Nigeria | tr. |
| S 14 | Kaolin | Skräbböle, Parainen, Finland | tr. < 0·027 |
| | | d) Tektosilicates | |
| S 99 | Quartz | Custer Mt., Black Hills, S. Dakota | |
| S 166 | Nepheline | (not known) | 7·6 |
| S 130 | Leucite | Civita Castellano, Italy | 65·0 |
| S 25 | Calcic Plagioclase | Hange, Egersund, Norway | tr. |
| S 9 | Calcic Plagioclase | Stillwater Complex, Montana | 0·029 |
| S 10 | Calcic Plagioclase | Stillwater Complex, Montana | 0·017 |
| S 181 | Bytownite | (not known) | — |
| S 40 | Albite | High Climb, Black Hills, S. Dakota | 2·0 |
| S 98 | Cleavelandite | Custer Mt., Black Hills, S. Dakota | 6·8 |
| S 126 | Amazonite | Woodcox Mine, N. Hastings Co., Ontario | 33·0 |
| S 100 | Microcline-Perthite | Custer Mt., Black Hills, S. Dakota | 84·0 |
| S 41 | Microcline-Perthite | High Climb, Black Hills, S. Dakota | 21·0 |
| | | e) Cyclosilicates | |
| S 125 | Beryl | Lyndoch Tp., Renfrew Co., Ontario | 0·40 |
| S 97 | Tourmaline | Custer Mt., Black Hills, S. Dakota | tr. < 0·031 |
| | | Igneous Rocks | |
| S 139 | Olivine rock | S. Massif, Khabozero, Kola Peninsula, U.S.S.R. | 0·11 |
| S 25 | Anorthosite | Hange, Egersund, Norway | tr. |
| S 9 | Anorthosite | Stillwater Complex, Montana | 0·029 |
| S 143 | Pyroxenite | Webster, N. Carolina | - |
| S 63 | Hornblendite | Kaalamo, Finland | — |
| S 21 | Peridotite | St. George, Garden Cove, Aleutian Is. | 0·13 |
| S 24 | Olivine-Basalt | St. Paul, Aleutian Is. | 0·026 |
| S 23 | Basalt | Tolstoi Point, St. George, Aleutian Is. | 0·019 |
| S 71 | Basalt | St. George, Aleutian Is. | 0·19 |
| S 90 | Basalt (carrying native iron) | Disco Is., Greenland | - |
| S 112 | Leucite-Basalt | Laacher See, Rheinprussen | 0·26 |
| S 113 | Tephrite | Rheinprussen | 0·16 |
| S 61 | Gabbro | Peuhkurinmaki, Parikkäla, Finland | - |
| S 137 | Gabbro | Sudbury, Ontario | 0·16 |
| S 140 | Gabbro | Virnikkasokka, Moskuvaara, Sodankylä, Finland | 0·060 |

*Table 2. (Continued)*

| *Sample Number* | *Sample* | *Locality* | Tl *ppm* |
|---|---|---|---|
| S 141 | Gabbro | Duluth, Minnesota | 0·058 |
| S 142 | Hornblende-Gabbro | Salem, Massachusetts | 0·46 |
| S 138 | Olivine-Diabase | Säppi, Luvia, Finland | 0·073 |
| S 57 | Diabase-Pegmatite | Säppi, Luvia, Finland | 0·47 |
| S 144 | Andesite | Mt. Shasta, California | — |
| S 145 | Diorite | Jersey City, New Jersey | 0·30 |
| S 147 | Monzonite | San Juan Co., Colorado | 1·7 |
| S 120 | Tonalite | Marquis Tp., Ontario | 0·29 |
| S 121 | Tonalite | Dack Tp., Ontario | 0·50 |
| S 22 | Dacite | St. George, Aleutian Is. | 0·51 |
| S 56 | Oligoclase-Granite | Orijärvi, Kisko, Finland | 0·42 |
| S 52 | Granite-Gneiss | Petäjäkylä, Pitkärantä, Finland | 2·8 |
| S 114 | Granite | Hangö, Finland | 6·4 |
| S 53 | Granite | Juva, Espoo, Finland (Bodom granite) | 4·8 |
| S 51 | Granite | Maarianvaara, Finland | 1·7 |
| S 49 | Granite | Sodankylä, Finland (Nattanen granite) | 1·5 |
| S 54 | Granite | Åva Brändo, Finland (Åva granite) | 2·3 |
| S 55 | Granite | Bomarsund, Ahvenanmaa, Finland (Rapakivi) | 4·0 |
| S 48 | Granite | Uuksu Salmi, K.F.S.S.R. (Rapakivi) | 3·0 |
| S 50 | Granite | Bamböle, Vehkalahti, Finland (Rapakivi) | 2·8 |
| S 92 | Pegmatite | Pyterlahti, Säkkijärvi, Finland (Rapakivi) | 33·0 |
| S 150 | Obsidian | Millard Co., Utah | 5·6 |
| S 149 | Obsidian | Lake Co., Oregon | 1·4 |
| S 29 | Granite Dyke | Albany Co., Wyoming | 1·5 |
| S 12 | Lamprophyre | Seabrook Lake, Mississagi Reserve, Ont. | 0·11 |
| S 59 | Lamprophyre | Åvo Brändö, Finland | 0·12 |
| S 118 | Syenite | Marquis Tp., Ontario | 1·1 |
| S 119 | Syenite | Marquis/Otto Tps., Ontario | 1·3 |
| S 146 | Phonolite | Cripple Creek, Colorado | 7·2 |
| S 164 | Nepheline-Syenite | Methuen Tp., Ontario | 2·2 |
| S 58 | Ijolite | Iivaara, Kuusamo, Finland | 1·4 |
| | | Sedimentary Rocks | |
| S 65 | Limestone | Limberg, Parainen, Finland | — |
| S 64 | Dolomite | Valkeamäki Tiutia, K.F.S.S.R. | — |
| S 148 | Arkose | Fair Haven, New Haven, Connecticut | 1·0 |
| S 93 | Sandstone | Huvitus, Yläne, Finland | 1·3 |
| S 91 | Phosphorite-Glauconite-Sandstone | Tallinn, Estonia | 0·17 |
| S 171 | Bauxite | Tennessee | — |
| S 17 | Laterite | Funchal, Madeira | 0·10 |
| S 38 | Greywacke | Manitou Lake, Ontario | 0·19 |
| S 37 | Greywacke | Mena, Arkansas | 0·21 |
| S 36 | Greywacke | Washington State, U.S.A. | 0·13 |
| S 2 | Loess | Farmdale, Illinois | 0·31 |
| S 1 | Varved Clay | Pembina Co., N. Dakota | 0·33 |
| S 15 | Clay | Mga River, Ingria, U.S.S.R. (Yoldia clay) | 0·24 |
| S 16 | Clay | Oulu, Finland (Ancylus clay) | 0·64 |
| S 8 | Shale | East Hoosick, New York | 0·14 |
| S 39 | Argillite | Dickinson Co., Michigan | 1·4 |
| S 13 | Shale (lime-rich) | Grayville, Illinois | tr. <0·14 |

*Table 2. (Continued)*

| *Sample Number* | *Sample* | *Locality* | Tl *ppm* |
|---|---|---|---|
| S 7 | Slate | Eagle Bridge, New York | 0·81 |
| S 174 | Pyritic Slate | Crystal Falls, Michigan | — |
| S 117 | Shale | Tallinn Estonia (Dictyonema shale) | 3·1 |
| S 66 | Phyllite | Tähtinen, Aitolahti, Finland (Corycium phyllite) | 0·79 |
| S 67 | Carbonaceous Schist | Beresford Lake, Manitoba | 0·60 |
| S 68 | Shungite | Veljakkala, Soanlahti, Finland | 0·11 |
| S 153 | Anthracite | Schuylkill Co., Pennsylvania | — |
| S 151 | Anthraxolite | Sudbury, Ontario | 2·8 |
| S 35 | Porcellanite | Iron Co., Michigan | 0·84 |
| S 4 | Rock Salt | Grand Saline Salt Dome, Texas | — |
| S 3 | Sylvinite | near Carlsbad, New Mexico | — |
| S 5 | Insoluble residue from Rock Salt | See S 4 | — |
| S 6 | Cap Rock | Hockley Mine Salt Dome, Texas | — |
| | | Deep-Sea Sediments | |
| S 103 | Manganese Nodule | 11° N; 113° 48′ W; depth 4090 m | 30–100* |
| S 104 | Volcanic Glass | 11° N; 113° 48′ W; depth 4090 m | 0·24 |
| S 105 | Iron-Manganese-rich Ooze | 07° 40′ N; 106° 21′ W; depth 3725 m | 0·3* |
| S 106 | Globigerina Ooze | 02° 44′ S; 92° 45′ W; depth 3600 m | 0·16 |
| S 107 | Deep-sea Clay | 15° 40′ N; 123° 21′ W; depth 4300 m | 1·5 |
| S 108 | Red Clay | 08° 25′ N; 128° 48′ W; depth 4610 m | 0·79 |
| S 109 | Siliceous Ooze | 03° 05′ N; 133° 06′ W; depth 4370 m | — |
| S 77 | Clay | 36° 16′ N; 70° 09′ W; depth 4500 m | 0·32 |
| S 78 | Clay | 37° 42′ N; 70° 53′ W; depth 3900 m | 0·62 |
| S 79 | Clay | 39° 25′ N; 69° 40′ W; depth 2480 m | 0·59 |
| S 80 | Clay | 39° 47′ N; 69° 42′ W; depth 1555 m | 0·16 |
| | | Metamorphic Rocks | |
| S 62 | Amphibolite | Impilahti, K.F.S.S.R. | 0·40 |
| S 26 | Norite Gneiss | Albany Co., Wyoming | tr. |
| S 27 | Diorite Gneiss | Albany Co., Wyoming | 0·42 |
| S 28 | Quartz Diorite Gneiss | Albany Co., Wyoming | 0·79 |
| S 30 | Quartz-Monzonite Gneiss | Albany Co., Wyoming | 0·74 |
| S 31 | Granodiorite Gneiss | Albany Co., Wyoming | 0·90 |
| S 110 | Granodiorite Gneiss | Egedesminde, Greenland | 0·72 |
| S 111 | Hornblende Gneiss | S. Stromfjord, Greenland | 1·1 |
| S 70 | Enderbite Gneiss | N. Isortog, Greenland | 0·10 |
| S 33 | Garnet Gneiss | N. Isortog, Greenland | 0·13 |
| S 32 | Garnet Gneiss | N. Isortog, Greenland | 0·37 |
| S 34 | Granulite Gneiss | N. Isortog, Greenland | 0·026 |
| S 155 | Olive Slate | Clove Quadr., New York | 0·60 |
| S 157 | Black Phyllite | Moores Mills, New York | 0·27 |
| S 156 | Black Phyllitic Slate | Clove Quadr., New York | 0·56 |
| S 158 | Biotite Phyllite | Clove Quadr., New York | 0·66 |
| S 159 | Biotite-Muscovite Phyllite | Clove Quadr., New York | 0·59 |

* Estimated by visual comparison.

*Table 2. (Continued)*

| *Sample Number* | *Sample* | *Locality* | Tl *ppm* |
|---|---|---|---|
| S 160 | Garnetiferous Schist | Clove Quadr., New York . . . . . | 1·1 |
| S 162 | Biotite-Garnet Schist | Clove Quadr., New York . . . . . | 1·3 |
| S 161 | Biotite-Hornblende Schist | Danbury Quadr., New York . . . . . | 0·35 |
| S 163 | Garnet Schist | Clove Quadr., New York . . . . . | 0·61 |
| S 176 | Sillimanite Schist | Clove Quadr., New York (Dark Layer) . . . | 1·9 |
| S 177 | Sillimanite Schist | Clove Quadr., New York (Light Layer from S 176) . . . . . | 0·74 |
| | | MISCELLANEOUS | |
| S 74 | Meteorite | Holbrook, Navajo Co., Arizona (Chondrite) . | — |
| S 75 | Meteorite | Norton Co., Kansas (Achondrite) . . . . . | — |
| S 76 | Meteorite | Plain View, Hale Co., Texas (Chondrite) . . | — |
| S 73 | Caliche | Chile . . . . . | — |
| S 81 | Ocean Salts | Woods Hole Harbour, Massachusetts; surface | — |
| S 82 | Ocean Salts | 34° 36′ N; 30° 00′ E; depth 750–1325 m . . | — |
| S 83 | Ocean Salts | 34° 36′ N; 30° 00′ E; depth 1500–1900 m. . | — |
| S 84 | Ocean Salts | 40° 15′ N; 25° 19′ E; depth 100–350 m. . . | - |
| S 85 | Ocean Salts | 40° 15′ N; 25° 19′ E; depth 350–750 m. . . | — |

## *Chemistry of thallium*

"Le thallium est destiné à faire époque dans l'histoire de la chimie par l'étonnant contrast qui se manifeste entre ses caractères chimiques et ses propriétés physiques. Il n'y a pas d'exagération à dire qu'au point de vue de la classification généralement acceptée pour les métaux, le thallium offre une réunion de propriétés contradictoires qui authoriserait à l'appeler le métal paradoxal, l'ornithorrhynque des métaux."

J. B. A. DUMAS.

It is necessary to mention very briefly some of the chemical properties of thallium, insofar as they are relevant to the geochemistry.

Thallium was discovered by W. CROOKES in 1861, who at first believed it to be an element similar to sulphur. The following year A. LAMY proved the new element to be a metal which forms two series of compounds, resembling lead on the one hand, and the alkali metals on the other. Later workers demonstrated resemblances also to gold and aluminium. Univalent thallium resembles both lead (in the sparing solubility of the halides and chromate) and the alkali metals (in the existence of thallia-alums and thallium chloro-platinate, and in the isomorphism of certain salts with those of potassium, rubidium and caesium).

In the periodic table thallium is now grouped with boron, aluminium, gallium and indium, having three valency electrons in the outer electron orbits and having certain properties similar to these elements when in the trivalent state.

The main features of thallium geochemistry stem from its resemblance to the alkali metals. For in most geological processes it is probable that thallium is in the reduced or thallous state, and replaces potassium in silicate minerals. This is due to similarities in ionic size, as exemplified by the following ionic radii:

$K^{+1}$ 1·33 Å
$Tl^{+1}$ 1·49 Å
$Rb^{+1}$ 1·49 Å
$Cs^{+1}$ 1·65 Å

This behaviour was recognised early in the present century. Later work by Ahrens suggested that nearly all of the thallium in the earth's crust is carried in potassium minerals, following the same distribution pattern as rubidium due to their identical ionic size. The results of the present work are in substantial agreement with Ahrens findings.

*Distribution of thallium in minerals*

In all the minerals analysed, thallium was present in trace quantities only, nowhere attaining the status of a major constituent. The analyses will thus be examined in accordance with the known principles of trace-element distribution. Minor elements follow distribution laws in the same manner as major elements; that is, the presence or absence of significant quantities of a trace element in a mineral depends on four main factors:

(a) the availability of that element when the mineral was formed;
(b) the chemical affinity;
(c) the ionic or atomic size;
(d) the valency.

When a crystal is growing in nature at least traces of almost all elements will be present in the general environment of the crystal, and so the absence of a given element in the mineral may be significant. The trace-element will enter a mineral according to the laws of isomorphism, and will be "camouflaged" by the major element whose equivalent position it can occupy. Which major element it will follow is determined primarily by its chemical affinity, and secondarily, by its ionic size and charge. The affinity depends mainly on the heats of formation of the oxides and sulphides, and the electronic configuration of the atom. Thus tellurium and zirconium have similar ionic radii in the tetravalent state ($Te^{+4}$ 0·89 Å : $Zr^{+4}$ 0·87 Å) yet tellurium is never reported as concentrated in zirconium minerals. The reason lies in the different affinities of the two elements. Full discussion of the camouflage principle may be found in several papers by Goldschmidt (*e.g.* [17]), and a brief summary will suffice.

A trace element of ionic radius ($r$) can substitute for a major element of radius ($R$) in a mineral when the two have the same valency and ($r$) is within $\pm 15\%$ of ($R$). If ($r$) is less than ($R$) the trace element will be concentrated in earlier fractions of the mineral, whilst if ($r$) is greater than ($R$) the reverse is the case. If the two ions are of similar size but different charge a substitution can again take place, provided that the charges can be balanced to preserve electrostatic neutrality. If the trace element has the higher charge it is concentrated in early fractions of the mineral, but if it has lower charge it accumulates in later fractions. It will be convenient to bear in mind the two ionic radii for thallium; viz, $Tl^{+3}$, 1·05 Å and $Tl^{+1}$, 1·49 Å.

The two samples of graphite analysed show a striking dissimilarity in thallium content. There seems little probability of thallium being present within the graphite structure, which consists entirely of carbon atoms, and the 0·49 ppm thallium in the Finnish specimen may be in an intimate intergrowth as some other thallium-bearing mineral. This specimen also shows a small but significant indium content (absent in the Ontario graphite): the ability of organic matter to accumulate heavy metals will be recalled (Goldschmidt [17]). The Ontario graphite is believed to

have formed by igneous contact processes, and it is possible that the Finnish graphite is of organic origin (see p. 127).

Among the oxides, the absence of thallium in quartz is to be expected, since quartz is one of the few minerals incapable of admitting trace elements in the usual case. The reason for this is structural, since cations must be tetravalent and of small size to replace silicon; ions of other valencies cannot usually substitute or else the electrostatic balance of valencies is destroyed, and there is little opportunity for a coupled replacement. In opal, on the other hand, a small amount of thallium is present; this mineral has a less rigid structure than quartz and may carry trace elements such as uranium and gallium (Rankama and Sahama [49] p. 635 and 722).

The iron oxide minerals appear to be uniformly low in thallium, with the exception of the Ontario magnetite which contains 0·36 ppm. As the host rock was rich in biotite, frequently in intimate intergrowth with the iron oxides, traces of this mica may account for the thallium. There is little likelihood of thallium occurring in the magnetite or hematite structures, as the radii of divalent and trivalent iron ions (0·83 Å and 0·67 Å respectively) are very different from either thallium ion. Pyrolusite, on the other hand is relatively rich in thallium (as far as could be judged by visual estimation of the spectra). Since the mineral was formed by sedimentary processes, the cause of this enrichment will be discussed later, but it is to be noted here that Hartley and Ramage [23] detected thallium in three manganese ores.

If the analyses of sulphides are reliable, the group chosen can hardly be said to emphasize the chalcophile tendencies of thallium. However the highest value is in galena, which has frequently been shown to carry thallium (*e.g.* Oftedal [42]). The distribution of thallium in sulphides needs detailed study, partly because the sulphides constitute economic sources for thallium and partly because sulphide minerals are sometimes notably enriched in thallium whilst at other localities they seem "barren". Thus Oftedal [42] quotes Goldschmidts opinion that thallium seldom occurs in pyrite. However, thallium is shown here to occur in a low concentration in marcasite, whilst Watanabé has found a marcasite in Japan to contain up to 0·03 % Tl. He mentions a possible suppression of thallium by iron in the arc, however, which may have led to erroneously low values in the past (see p. 126). Other references in the literature are not very satisfactory however. Thus Zakharov and Yushko [69] discuss the distribution of thallium in the base-metal ores of the Urals, reaching no definite conclusions as to which sulphides carry most thallium. They believe however that the presence of thallium is connected with the copper-zinc mineralization. No analyses are given, though spectrographic work was carried out. Rusanov and Alekseeva [52] have determined thallium in chalcocite and sphalerite but their paper is concerned with methods. Novokhatskii and Kalinin [40] showed thallium to be present in galena-pyrite and galena-marcasite aggregates. Murakami [37] analysed numerous minerals by chemical and spectrographic methods, finding that marcasite, enargite, sphalerite and native bismuth contain up to 0·1 % Tl.

Stoiber [60] found thallium only in low-temperature sphalerites from the Belgium-Westphalia-Silesia deposits, where a semi-quantitative method showed up to 1 % Tl was sometimes present. Similar low-temperature sphalerites from the

Mississippi valley showed no detectable thallium, suggesting the existence of a geochemical province in North-central Europe characterised by a relative abundance of thallium.

The only minerals containing essential thallium are the following very rare sulphides:

| | |
|---|---|
| Lorandite | $Tl_2S \cdot As_2S_3$ |
| Crookesite | $Cu_{15}Tl_2AgSe_9$ |
| Vrbaite | $Tl_2S \cdot 2As_2S_3 \cdot Sb_2S_3$ |
| Hutchinsonite | $PbS \cdot (Ag, Tl)_2S \cdot As_2S_3$ |

Thallium was not detected in any of the halides. With fluorite the spectral line would be obscured by an intense CaF band spectrum. One would not expect trivalent thallium to be captured in fluorite, however, in spite of the close similarity in radii ($Tl^{+3}$ 1·05 Å:$Ca^{+2}$ 1·06 Å), as the fluorine could not be replaced by other ions of lower valency. With the alkali halides the large amounts of alkalies gave rise to considerable arcing difficulties and the results are unreliable. Nevertheless there can be very little thallium present in these salts, which is significant, since one might expect some replacement of potassium ($K^{+1}$ radius 1·33 Å) by univalent thallium as is found in potassium silicates. Rankama and Sahama ([49], p. 728) do in fact record that thallium has been found in sylvite and carnallite. At the (geologically) very low temperatures at which these evaporite minerals form, they must be regarded as rather intolerant to substitutions of foreign ions. This intolerance is shown by the lack of any considerable replacement of sodium in sylvite (KCl), whereas at higher temperatures the alkali feldspars show a complete series of solid solutions (however see Bowen and Tuttle [9]). It is interesting to note that rubidium (with the same ionic size as univalent thallium) is present in carnallite ($KCl \cdot MgCl_2 \cdot 6\,H_2O$). (Goldschmidt, Bermann, Hauptmann and Peters [20]). It is probable that more rubidium would be present in these evaporites if most of it had not been removed by adsorption in clays, and similar reasoning may be applied to the lack of thallium. We may note, however, that the compound TlCl differs from KCl in having low solubility, and so any thallium remaining in sea-water will be quantitatively precipitated during evaporation.

The apatite sample showed a small content of thallium. This was probably captured in the trivalent state, replacing calcium.

The nesosilicates have low but varying thallium contents. It is surprising that the olivine-rock from Kola contains any thallium, for olivine seldom permits substitution of trivalent ions, as coupled replacement does not take place in this mineral. It is possible, of course, that the thallium is present in some other mineral. On the other hand it is surprising that garnets should contain so little thallium, since the trivalent ion is of the correct size to substitute for calcium—a possibility put forward by Ottemann [43] who also noticed the absence of thallium in epidote. The zircon specimen is surprisingly high in thallium, which is difficult to understand since the radius of $Zr^{+4}$ (0·87 Å) is very different from thallium.

Titanite contains a trace of thallium, presumably in a trivalent state, replacing calcium. This mineral is a potent storehouse of trace-elements, as has been shown by Sahama [55] and others.

The pyroxenes have only a limited tolerance to large ions which require eight-fold co-ordination or greater. Thus calcium is present only in the monoclinic varieties as an essential element, and the ortho-pyroxenes will tolerate little calcium at all, their cations all being in the "Y-group" (*i.e.* the $Mg^{+2}$—$Fe^{+2}$ size range). These minerals have negligible thallium contents, and the only figure is from the Ontario augite. By contrast the amphiboles have a greater flexibility, both as regards valency and radius considerations, having a "defect-structure" in which vacant lattice positions can be tolerated. This demonstrated by the appreciable values for thallium. In both groups the thallium is probably in the trivalent state, replacing calcium (radius 1·06 Å) in the "X-group" (*i.e.* the $Na^{+1}$—$Ca^{+2}$ size range).

In the phyllosilicates it is not surprising that kaolin and chlorite have negligible thallium content, as their cations are small. But with the micas, having the greatest flexibility of all silicates for accommodating trace elements, the reverse is true. All the micas analysed are very rich in thallium, which is in the monovalent state replacing potassium (see Ahrens [5]). Due to the radius difference one expects an enrichment of thallium in late stage micas, and this is shown by the Black Hills muscovite and lepidolite (pegmatitic), where the content is up to 95 ppm. A large number of micas have been analysed for thallium by Ahrens [5], and the values recorded here fall within the concentration ranges he found for lepidolite (50 to 268 ppm Tl) and muscovite (1·9 to 144 ppm Tl). The phlogopite from Skräbböle is extremely rich in thallium, however, containing 78 ppm: Ahrens found a range from less than 1 to 4·4 ppm only, which is to be expected, since phlogopitic micas are formed either in basic pegmatites or metamorphosed dolomites, both environments being poor in alkalies and thallium. This suggests that the thallium-rich mica Skräbböle is not a true phlogopite, and is from a granite pegmatite. Biotites show an extremely wide range in thallium concentration. Thus Ahrens [5] found values of 80 and 384 ppm, whilst Ottemann [43] found values of 4 and 100 ppm. This wide range in values is consistent with the variation in composition of biotites formed in different environments.

The tektosilicates form a group with related structures which may be regarded as derived that from of quartz. As previously mentioned the absence of thallium in quartz is consistent with structural considerations. Nepheline contains quite a high content of thallium. As nepheline constitutes a limited solid solution between $NaAlSiO_4$ and $KAlSiO_4$, it is probable that the thallium is univalent and replaces potassium. For the trivalent thallium ion, though smaller, would be unlikely to replace univalent sodium, as it would not be possible to effect a coupled substitution to balance the valencies without contravention of Paulings rules. The size difference between the major ion ($Na^{+1}$, 0·98 Å) and the trace element $Tl^{+1}$, 1·49 Å) amounts to more than 50%, and demonstrates considerable flexibility in the nepheline structure.

The high thallium content of leucite is consistent with the replacement of potassium by univalent thallium, as noted by Goldschmidt [18], who found leucite to contain from 3 to 20 ppm. However, certain leucite-rich rocks contain much less thallium than one might expect (see later).

Among the plagioclase feldspars thallium increases with the sodium content, the calcic varieties being very low in thallium. This may be due principally to one of two reasons. Firstly monovalent thallium will not easily substitute for calcium

due to size and valency differences, and secondly the trivalent ion will also have difficulty in substituting for calcium, in spite of very similar radii. In the latter case one must conceive of the existence of a compound such as $TlAl_3SiO_8$ in solid solution with $CaAl_2Si_2O_8$. But this thallium-anorthite would have more than half of the Si ions substituted by Al ions, which is in contravention of a rule of crystal chemistry formulated by Pauling. It is unlikely therefore that the thallium in basic plagioclase is in the trivalent state, although this was suggested by Ottemann [43]. It is more likely to be present as the compound $TlAlSi_3O_8$—*i.e.* replacing potassium or sodium. Potassium is closer in radius to thallium, and the two will thus form a more coherent pair. In Wickmans phraseology [66] thallium will have an *E*-value lower than potassium and much lower than sodium, in the high co-ordination of the feldspars. Then early magmatic plagioclase contains little sodium, and will contain proportionately less potassium and thallium, as shown by the analyses here. The albitic plagioclases however are richer in thallium, showing comparable values to nepheline, and to the values for these minerals found by Ottemann [43] and Ahrens [5]. It was expected that among the feldspars the late-stage potash minerals would be rich in thallium, and the specimens analysed here represent this pegmatitic enrichment stage. Ahrens [5] made numerous analyses of potash feldspars from normal magmatic, early pegmatitic and late pegmatitic stages, and there is by no means the same high thallium content in the earlier minerals. Thus three orthoclases from granites average only about 0·8 ppm Tl, and out of 55 early pegmatite potash-feldspars only one has more than 10 ppm Tl. Later feldspars however are strongly enriched. Similar results were found by Ottemann [43]. The ratio of Tl/K is not a constant in the feldspar, but increases with decreasing temperature. Here then is another reason why the basic plagioclases are so impoverished in thallium, and this has some bearing on the derivation of figures for the crustal abundance of thallium (see p. 147).

The low thallium content of tourmaline is surprising. The analysed specimen is from a pegmatite, where other minerals rich in thallium were formed, and tourmaline contains cations of a wide size range, though potassium is usually low. Ottemann [43] also comments on the low thallium content of tourmaline.

In the cyclosilicates beryl has a relatively high thallium content. Böse [8] did not record the presence of thallium in any of the numerous beryl samples he analysed though many other trace-elements were found. Ahrens [5] however found 38 ppm Tl in a Madagascar beryl which was extremely rich in caesium. These trace elements are probably not concealed in the structure by substitution. Beryl has a "cylindrical" structure with vacant spaces among the rings of silicon-oxygen tetrahedra and it is believed that trace elements may occupy these "holes" (see Rankama and Sahama [49], p. 120).

Certain other minerals are interesting in connection with thallium geochemistry. Thus pollucite ($CsAlSi_2O_6.H_2O$) has been shown by Ahrens ([3], [5]), to be enriched in thallium up to 106 ppm, and the very rare rhodizite ($KNaLi_4Al_4 . Be_3B_{10}O_{27}$) was found to contain 96 ppm. Novokhatskii and Kalinin [41] have recorded 100 ppm in pollucite and 200 ppm in damourite (a variety of muscovite).

We may summarise the behaviour of thallium in the silicates in the following manner. Thallium enters silicates almost entirely as the large monovalent ion. It has a high co-ordination number, seldom (if ever) less than eight, so that it is typically

associated with the alkali metals of large ionic radius. We must regard its $E$-value in sixfold co-ordination as extremely low, so that there is little tendency for it to be bound in the olivines and orthorhombic pyroxenes, and when it occurs with the alkalies, as in micas and feldspars we have

$$E_{\mathrm{K}} > E_{\mathrm{Tl}} = E_{\mathrm{Rb}} > E_{\mathrm{Cs}}.$$

Studies by AHRENS [5] show that rubidium and thallium are geochemically very similar, as their similar ionic radii suggest, so we may assume their migration energies to be similar (however, see p. 149). It is evident that the relation of $E$-values expressed above explains the tendency for thallium to be enriched in late-stage pegmatitic minerals, at lower temperatures.

In a very few minerals, such as titanite and amphibole, a little thallium is present in the trivalent state, where it is presumably in eightfold co-ordination. The amount of this "oxidised thallium" is however very small.

*Distribution of thallium in rocks*

In the preceding section the abundance of thallium in the principal rock-forming minerals, as well as other minerals, has been considered from the viewpoint of crystal chemistry. The distribution of trace-elements in rocks is controlled once again principally by considerations of crystal chemistry, but also by certain other geochemical processes which will be considered in due course.

Calculations are presented later which show that the mean abundance of thallium in igneous rocks is 1·3 ppm. In the following pages this figure will be understood to be the reference when a rock is said to be "enriched" or "impoverished". The igneous rocks will be considered first.

*Igneous rocks*

The figures obtained are in entire agreement with the conclusions reached on the incorporation of thallium in the silicates. Thus the basic and ultra-basic rocks are composed in the main of pyroxene, olivine, amphibole and basic plagioclase, and none of these rocks contain appreciable thallium. Yet the monoclinic pyroxenes and amphiboles should theoretically be able to carry abundant trivalent thallium, and its absence we must ascribe to the strong reducing conditions characterising the formation of these rocks, shown especially by relatively high ratios of $Fe^{+2}/Fe^{+3}$. The higher value of 0·26 ppm in the leucite-basalt from the Rhine is in accord with the camouflage of thallium in potassium silicates. However the rock is seen in thin section to be rather rich in leucite, so this mineral must contain a great deal less thallium than the leucite specimen from Civita Castellano, which contained 65·0 ppm. The reason lies in the fact that the $E$-value for potassium in leucite is greater than for thallium, so that the high-temperature leucite of the basalt would be unable to take in as much thallium as the large single crystal from Civita Castellano, formed probably at a much lower temperature.

Another high value for a basic rock is 0·46 ppm for the hornblende gabbro from Salem, Massachusetts. Apparently some trivalent thallium must have been present during formation of the rock, and is no doubt camouflaged in the amphibole.

The figures for basic rocks are mostly somewhat lower than the figure of 0·3 ppm obtained by PREUSS [45] as the mean of eleven German gabbros.

The rocks from Säppi, Finland (S 138.57) represent the parent and end product in a common differentiation process of basaltic magma. The well-known enrichment of the alkalies in later liquids is seen to be accompanied by a slight thallium enrichment also, as would be expected. On the other hand the diabase pegmatite contains much less than granitic rocks. It must be concluded that this type of basalt differentiation does not give a magma which can consolidate to the ordinary thallium-rich granites, assuming the Säppi rocks to be representative.

The intermediate igneous rocks are also low in thallium, compared with the mean igneous value, with the exception of the Colorado monzonite, which is relatively richer in potash. However there is a large jump in values once the granite group is reached, and the average granite contains 3·1 ppm—more than double the average igneous rock. The Rapakivi granites are richer than most.

Some figures for granitic rocks obtained by previous workers are presented in Table 3, and show general agreement with the range of values found here.

The sodium-rich syenites and feldspathoidal rocks are also enriched in thallium, though not as much as the granites, although the Colorado phonolite has the highest value for an igneous rock (excluding pegmatite). This is in accordance with an origin by differentiation of magma leading to soda-rich rocks with relatively little enrichment in potash and hence in thallium. If igneous rocks are all to be considered as derived from a parental basaltic magma, then in the development of the sodium-rich line of differentiation the alkalies of large ionic radius must have gone elsewhere.

The rather heterogeneous group of rocks known as lamprophyres have been described as originating by mixture of early formed basic minerals and a late-stage magmatic residuum. If this is true for the examples analysed here, then the later magmatic liquids cannot have been appreciably enriched in thallium. The Seabrook Lake rock is rather rich in biotite, and so its low thallium content (0·11 ppm) is surprising.

The Rapakivi pegmatite from Finland is a quartz-feldspar rock which represents the last stage of ordinary magmatic crystallisation, if not the earliest in hydrothermal conditions. The sample analysed may not be representative, but shows the very strong enrichment in thallium of potassium minerals formed at this stage, as is also shown in the table of mineral analyses. Moreover Zies [68] found thallium deposited with molybdenum in fumaroles in Alaska associated with the late-stage igneous activity at Katmai, which is in agreement with the accumulation of thallium in the rest-magma. Similar fumarolic deposition of thallium has been noted at Stromboli in the Tyrrhenian Sea [47]. It is appropriate here to consider as a group the pegmatite minerals from Custer Mt., Black Hills, South Dakota*. These come from the Custer Mountain Lode, which has been described by Fisher [14]. The age relations of the seven minerals concerned are indicated below (Fishers Table 1, simplified).

| *Early* | | *Middle* | *Late* | |
|---|---|---|---|---|
| Tourmaline | tr. ppm Tl | Apatite 0·23 ppm Tl | Cleavelandite | 6·8 ppm Tl |
| Muscovite | 47·0 ppm Tl | | Lepidolite | 95·0 ppm Tl |
| Microcline | 84·0 ppm Tl | | | |
| Quartz | n. d. ppm Tl | | | |

* Numbers S 97, 102, 100, 99, 101, 98, 96 in Table 2.

These minerals are the products of late-magmatic and (possibly) hydrothermal crystallisation, and indicate the enrichment of thallium in the rest-magma. In particular we may note that the potash feldspar occurring with muscovite is enriched in thallium compared to the latter mineral. AHRENS found these minerals to have similar values ([5], Table 4). Moreover between the two micas, the later lepidolite is much enriched in thallium. It is notable that almost all the thallium is contained in the potash minerals, although some is present in cleavelandite. AHRENS found no detectable thallium in albites from pegmatites.

Many thallium compounds are readily volatile, and it was considered possible that volcanic rocks might contain less than plutonic rocks, due to loss of volatiles. Inspection of the analyses does not bear this out, indicating that conditions during extrusion did not permit the loss of thallium. The amount deposited in fumaroles is no doubt negligible.

The thallium contents of igneous rocks are consistent with theories of magmatic differentiation. When basaltic magma crystallises the early-formed minerals contain little potassium and hence little thallium. As crystallisation proceeds thallium is stored up in the liquid, so that basalts contain an average of 0·135 ppm only (Table 3). Later fractions solidifying to granite contain an average of 3·1 ppm. The late-magmatic liquids become notably enriched and some pegmatitic potassium minerals contain up to 100 ppm. This sequence is governed by the size and charge relations of the cations. Whether the distribution can be explained by other processes will be considered later.

The average values for igneous rocks are presented in Table 3, along with some figures from the literature.

*Table 3. Average thallium content of igneous rocks*

| | Tl *ppm* |
|---|---|
| Peridotite and Pyroxenite (4 samples) | 0·060 |
| Anorthosite (2 samples) | 0·015 |
| Basalt (4 samples) | 0·124 |
| Gabbro (6 samples) | 0·135 |
| Diorite and Andesite (2 samples) | 0·15 |
| Granodiorite and Tonalite (4 samples) | 0·43 |
| Syenite and Monzonite (3 samples) | 1·4 |
| Granite (10 samples) | 3·1 |
| Rhyolite Obsidian (2 samples) | 3·5 |
| Nepheline Rocks (3 samples) | 3·6 |
| German Gabbros (PREUSS [45]) | 0·3 |
| Granites and Liparites (GOLDSCHMIDT and HÖRMANN in GOLDSCHMIDT [18]) | 0·5—1·0 |
| German Granites (PREUSS [45]) | 3·0 |
| Harz Granites (OTTEMANN [43]) | 1·5 |

*Sedimentary rocks*

During the course of magmatic evolution the principal factors governing the distribution of elements are valency and size. Whilst these remain of prime importance during erosion and sedimentation other chemical and physical properties are also significant.

The influence of ionic charge ($Z$) and radius ($r$) during sedimentation are best shown by their quotient, known as the "ionic potential" ($P$).

$$i.e. \quad P = \frac{Z}{r}.$$

Thus Goldschmidt [17] divides the elements into three principal groups on the basis of their ionic potentials:

*I Elements of low ionic potential*

During weathering these remain in true solution as cations, and may be carried down to the sea.

*II Elements of medium ionic potential*

These are readily hydrolysed and are likely to be precipitated as hydrated oxides. Aluminium and iron are typical examples, commonly forming bauxite and laterite deposits.

*III Elements of high ionic potential*

These form complex anions with oxygen, including the typical acid radicles, and usually remain in solution.

We note here that monovalent thallium has a low ionic potential (0·67) placing it in Group I, and will return to this later.

The ionic potential obviously differs for ions of an element in different valency states, and it is necessary to consider the operation of oxidation-reduction reactions during weathering and sedimentation. Excellent papers by Scerbina [56] and Mason [35] have explored this field, pointing out the importance of redox potential values in sedimentary processes. At the temperatures and pressures of formation of igneous rocks there is insufficient oxygen available for complete oxidation of some metals. This is evident especially in the relations between $Fe^{+2}$ and $Fe^{+3}$, as has been stressed by Goldschmidt [19]. Once these rocks are exposed to weathering however, abundant oxygen is available, and whether oxidation of a given metal ensues depends on conditions in aqueous solutions. The redox potential for the thallous-thallic couple at $p_H = 0$ and at 25° C in aqueous solution is given below (Latimer [31])*.

$$Tl^{+1} = Tl^{+3} + 2e \qquad E_0 = +1{\cdot}25 \text{ v}.$$

This means that thallic thallium is a stronger oxidising agent than hydrogen, which has a redox potential of 0·00 v at 25° C. The potentials vary with the nature of the solution, in particular with $p_H$ values.

Redox potentials decrease as $p_H$ increases. Since sedimentary processes take place in aqueous environments the only oxidation-reduction reactions which can take place are those with potentials within the limit of values for oxidation and reduction of water. These limits are theoretically 1·23 v and 0·00 v (at $p_H = 0$), but in practice the range is somewhat grater due to overvoltage phenomena. Moreover, the $p_H$ values of natural waters vary, but they are seldom strongly acid or strongly

* Latimer uses the opposite sign convention for redox potentials to Mason; usage of the latter is followed here.

alkaline. For $p_H = 7$ the values are changed to 0·82 v and −0·41 v respectively, with a range of 1·23 v still. Certain relevant values follow, for $p_H = 0$:

$$Fe^{+2} = Fe^{+3} + e \qquad E_0 = 0{\cdot}77\,\text{v.}$$
$$Mn^{+2} + 2H_2O = MnO_2 + 4H + 2e \qquad E_0 = 1{\cdot}28\,\text{v.}$$
$$Tl^{+1} = Tl^{+3} + 2e \qquad E_0 = 1{\cdot}25\,\text{v.}$$

It is evident that an environment with a certain redox potential could oxidise iron but not manganese. Both these elements tend to be precipitated as hydrated oxides, when oxidised, usually giving rise to deposits containing limonite and psilomelane. Deposits of this kind consist mainly of limonite or else contain both iron and manganese: this is in accord with the redox potentials, which indicate that the latter formed under stronger oxidising conditions. Some relevant analyses from the main tabulation are presented in Table 4. Although the last three values in Table 4

*Table 4. Thallium in hydrolysates*

| *Sample Number* | *Sample* | *Locality* | Tl *ppm* |
|---|---|---|---|
| S 19 | Limonite | Haapakylä, Evijärvi, Finland . . . . . | tr. |
| S 17 | Laterite | Funchal, Madeira . . . . . | 0·10 |
| S 105 | Iron-Manganese-rich ooze | Pacific Ocean . . . . . | 0·30 |
| S 170 | Pyrolusite | (not known) . . . . . | 1·0 |
| S 103 | Manganese Nodule | Pacific Ocean . . . . . | 30—100 |

were estimated by visual comparison, it is clear that thallium is enriched considerably in manganese-rich environments, corresponding to strong oxidising conditions, whilst the potential of formation of hydrated iron oxides alone is insufficient to precipitate thallium. This is in accord with the redox potentials given above and the low solubility of thallic hydroxide. Thus thallium will be enriched (when available) in strong oxidising environments. The lack of any thallium in the Chilean nitrates (S 73) indicates that no thallium was available when these deposits formed, as otherwise it would certainly have been deposited under these extreme oxidising conditions, unless a salt more soluble than potassium nitrate was present, which is unlikely.

However, the high redox-potential of the thallous-thallic couple indicates that in normal weathering and sedimentation processes only the thallous ion will be present. The appropriate ionic potential is 0·67 and thallium will be carried in solution as the monovalent cation.

If other factors did not operate, one would expect thallium to be carried down to the oceans after erosion, apart from that trapped in sediments formed under strong oxidising conditions. The ubiquitous presence of thallium in shales indicates that another process must have operated, this being ionic sorption.

Clay sediments are chiefly alumina and silica, transported to some extent in colloidal solution, and colloids have the ability to adsorb cations. Which cations are adsorbed depends on several factors, but the large alkali ions are preferentially enriched in this way in most argillaceous sediments, being thereby impoverished in the oceans. The initial incorporation of cations is due to surface electrostatic effects

which may be truly called "adsorption". During the lithification of these sediments however, the clay minerals and micas are formed, and in some of these (*e.g.* illite) a large alkali ion—principally potassium—seems structurally necessary. This process would be better known as "chemisorption".

Thallium behaves in this regard in the same way as rubidium so long as it remains in the monovalent state, and thus is removed almost entirely from solution, and incorporated in the argillaceous sediments. This is demonstrated by the presence of appreciable thallium in these sediments, and its apparent absence in ocean-water residues. Thus the average argillaceous sediment contains 0·69 ppm (see Table 5). It is unlikely that thallium is precipitated as a chloride from river water, for although TlCl is only sparingly soluble (0·33 gms in 100 gms $H_2O$ at 20° C) the concentration of this salt is extremely low.

The bauxite analysed (S 171) contained no thallium, which is no contradiction to sorption processes. For the aluminium hydroxide sol has a negative charge, and has no appreciable power to adsorb cations, unless its charge is neutralised in some way. This may occur by mixing with a positive silica sol, but this gives rise to the clay mineral deposits rather than the hydrated aluminium oxides, which compose bauxite. Flocculation of the aluminium sol alone seldom allows ordinary sorption to take place.

The six samples S 117, 66, 67, 68, 151, 153 all contain free carbon or hydrocarbons mixed with varying amounts of sediment. All are therefore characterised by having formed under strong reducing conditions, varying between the black-shale facies and the coal-swamp facies. Their average thallium content is 1·23 ppm, a value nearly twice as high as the average argillaceous sediment (see Table 5). This indicates the tendency for thallium to be enriched in the strong reducing environments where organic material is accumulating in quiet, anaerobic conditions. It is entirely possible that the organic material itself contributed some of the extra thallium, by the continued processes of accumulation, reduction and leaching of soluble material. These processes have been sugested to account for the considerable enrichment of elements such as germanium in coal ash (Goldschmidt [17]), and the elements concerned are probably precipitated as sulphides. If this be so, some interesting deductions can be made*.

It seems that these sediments owe their increased thallium content to organic action, and probably the same is true of the graphite S 69. All except the Dictyonema shale and the Anthracite are of pre-Cambrian age, and in particular the Corycium phyllite and the Beresford Lake schist are of Archean age. It must be concluded therefore, that organic material has been present on the earth since Archean times. This has been suggested for the Corycium rock before, and recently revived by Rankama [48], from isotopic data. The nature of the organic matter is obscure, but may have been algal material, as suggested for Corycium.

Arenaceous deposits are not well represented here. Since they consist of sandstone, arkose and conglomerate types one expects a wide range in thallium content with the highest figures in arkose derived from a granitic terrane, and the lowest in the pure orthoquartzites. The average of three sediments of this nature (S 148, 93, 91) is 0·82 ppm. Greywackes represent a mixture of sandstone, limestone and

* The anthracite apparently contains no thallium, but has a low ash value compared with the other samples.

clay sediments, roughly speaking, and might be excepted to be intermediate in value. The average of three greywackes is 0·18 ppm which is rather low.

The absence of any determinable thallium in the limestone and dolomite analysed is to be expected. Both rocks were highly pure carbonates, and no appreciable thallium is present unless there is an abundance of clay material also, as in the lime-rich shale from Grayville Illinois (S 13), which shows only a trace.

The average values obtained for sedimentary rocks are presented in Table 5. along with some figures from the literature.

*Table 5. Average thallium content of sedimentary rocks*

| | Tl *ppm* |
|---|---|
| Clay and Shale (18 samples) | 0·69 |
| Carbonaceous Shale (6 samples) | 1·23 |
| Limestone and Dolomite (2 samples) | — |
| Arkose and Sandstone (3 samples) | 0·82 |
| Greywacke (3 samples) | 0·18 |
| German Shales (PREUSS [45]) | 2·0 |
| German Sandstones (PREUSS [45]) | 2·0 |

The figures of PREUSS refer to 36 and 23 sandstones, and are considerably higher than the averages in the present study. Whether this is due to experimental inaccuracy in one or other of the methods, or whether it arises from a geochemical peculiarity in the rocks used is not apparent. The higher figure for sandstones gives no cause for concern, for two reasons. First of all only three such samples were analysed in the present work, and so their average has no value statistically. Secondly, a very small amount of pegmatitic alkali feldspar incorporated in a sandstone could increase the thallium content considerably. With the shales, however, there is a serious conflict in the results. In both cases sufficient samples were used to give a good average. Moreover, shale material has been thoroughly sorted and broken down from its previous existence as igneous material and so chance accumulation of thallium-rich minerals would be very unlikely. The spread of values for shales in this work was from 0·00 to 3·1 ppm, although the only sample with a value greater than 1·4 ppm was considerably enriched in organic matter. In view of these rather consistent results the present figures are considered likely to be representative.

The writer was fortunate in obtaining sundry marine waters and deep-ocean materials, which are considered next.

The ocean water samples were evaporated to obtain the solid residues, which were then analysed in the usual manner (but see p. 130–1). In no case could thallium be detected, and in spite of uncertain experimental conditions this must indicate the lack of thallium in concentrations greater than perhaps 0·6 ppm in the residue, or about 0·02 ppm in sea-water. Recalling the similar behaviour of rubidium and thallium during sorption by clays, one might expect the ratio of their amounts in sea-water to be of the same order as in igneous rocks, that is, of the order of 100:1 (AHRENS [5]: but see p. 139). The rubidium content of sea-water is given by HARVEY [24] as 0·2 ppm and so we might expect only about 0·002 ppm thallium. However, even this minute quantity is apparently of biological significance, as RANKAMA and

Sahama ([49], p. 728) report its occurrence in marine animals. Moreover, several authors have found thallium in minerals such as carnallite and sylvite which formed as evaporites. This may be due to some enrichment process arising from the low solubility of thallous chloride.

The four clay sediments S 77 to 80 were used in the compilation of the average clay and shale composition, and represent the west Atlantic deep and continental shelf. The average thallium content is 0·42 ppm which is a little lower than normal shallow-water sediments. This is to be expected, for most of the thallium in river waters draining the continents will be adsorbed close to the sea-coast where clay colloids are flocculated. These deep-ocean sediments are in part derived from volcanic ash, which would contribute a little thallium.

The Pacific Ocean samples are of varying nature. Of the fine-grained sediments the lowest thallium contents are in the oozes, which represent clay materials "diluted" by organic remains of a siliceous (S 109) or calcareous (S 106) nature. The volcanic glass has a value appropriate to an intermediate rock. The ooze rich in iron and manganese (S 105) has a fairly high value, and the manganese nodule appears very rich in thallium. This nodule probably formed in an oxidising environment by circulating solutions in the sediments (G. Arrhenius: personal communication), and such an explanation would adequately account for the enrichment in thallium (see p. 141).

### *Metamorphic rocks*

Very little systematic study of the trace-elements in metamorphic rocks has been carried out, and this is a difficult field in geochemistry. In studying the course of metamorphism one follows the changes in a given rock with varying pressure and temperature. In any chemical work it is always difficult to be sure that schists of different grades do in fact represent the same original stratum. Unless this is assured, it is usually useless to try to compare trace-element analyses.

The amphibolite (S 62) shows a thallium content of 0·40 ppm. This may be contrasted with the hornblendite (S 63) in which no thallium could be detected. This might be expected since hornblendite is believed to represent early magmatic accumulation. At that stage, the magma would have had a very low thallium concentration which one would expect to be indicated by the low content in hornblendite, in spite of the capture of $Tl^{+3}$ by $Ca^{+2}$ in the amphibole.

On the other hand the amphibolite is a metamorphic rock. If it represents a chemically unaltered basic rock the thallium content is rather high, but if it represents a chemically altered basic rock or a tuff, or alternatively is perhaps dioritic or andesitic the higher value might be expected. Frequently it is not possible to judge whether these hornblende-rich rocks are metamorphosed basic rocks, lime-rich sediments or primary magmatic segregations, and it may be that trace element analyses such as these could provide criteria for deciding. It is very likely that similar appearing rocks of entirely different original constitutions may show significantly different trace element contents, and investigation of this problem might provide diagnostic information. In the present case two analyses are quite insufficient to suggest whether thallium would be a valuable index or not.

The rocks from Dutchess county, New York (Balk and Barth [7]), come from an area which has been studied in considerable detail. Some of the samples were

*Table 6. Thallium content of Dutchess county pelitic sediments*

| *Number* | *Rock type* | Tl *ppm* |
|---|---|---|
| S 155 | Olive Slate, anal. 3, p. 799* | 0·60 |
| S 157 | Black Phyllite: anal. 2, p. 799 | 0·27 |
| | Average S 155, 157 | 0·44 |
| S 156 | Black Phyllitic Slate: anal. 4, p. 799 | 0·56 |
| S 158 | Biotite Phyllite: anal. 5, p. 802 | 0·66 |
| S 163 | Garnet Schist: anal. 9, p. 804 | 0·61 |
| S 160 | Garnetiferous Schist: anal. 7, p. 802 | 1·1 |
| S 176 | Sillimanite Schist: anal. 12, p. 812 | 1·9 |
| S 177 | Pegmatitic Vein from S 176 | 0·74 |

* Analysis and page numbers refer to Balk and Barth [7].

chosen by Dr. Balk to represent the same pelitic sediment at various degrees of metamorphism. These analyses are arranged in Table 6, in order of increasing metamorphism, excepting the first two, which are both in the lowest grade.

The lowest grade of metamorphism (equivalent to the chlorite grade in the Scottish Highlands) includes the first two examples. The next three are in the biotite zone, S 160 is at the staurolite isograd and the last two are in the sillimanite zone.

It would perhaps be unwise to take so small a number of analyses as indicative of a definite trend, but it seems nevertheless that these figures demonstrate a thallium increase, during increase in metamorphic grade: *i.e.* although the series is isochemical (roughly) with regard to major constituents it is not so as far as one trace constituent is concerned. Moreover, the thallium content of the low-grade rocks is close to the average argillaceous sediment (0·69 ppm), suggesting that the high-grade rocks have become enriched from without, and not by transfer of material from low to high grades. The quartzo-feldspathic vein from the sillimanite schist is lower in thallium than its host rock, suggesting that the liquids which introduced this vein material also added thallium to the host rocks, leaving a deficiency in the injection veins themselves. It seems that the figures suggest a "thallium metasomatism", though admittedly on a rather modest scale.

Samples S 159, 161, 162 were not typical of the pelitic series, and thus have not been discussed.

We turn now to the gneisses of Albany County, Wyoming, which are being studied by W. H. Newhouse, A. F. Hagner and G. de Vore. The five samples S 26, 27, 28, 30, 31 and the granite dyke S 29 are believed to constitute a related series of rocks derived from the metanorite by mainly metasomatic reactions. The thallium content shows an increase from almost zero to 1·5 ppm in the granite dyke. This seems characteristic of other calcalkalic suites and is demonstrated by the average figures for igneous rocks (Table 3). That such an increase would be expected in a magmatic origin has been demonstrated earlier, but the previous remarks about the Dutchess County rocks allow the possibility that plutonic metamorphic processes might conceivably lead to the same results.

The six rocks from Greenland are from an area being studied by H. Ramberg. They are pre-Cambrian gneisses of a silicic nature, some members having charnockitic affinities. Their chemical analyses show some differences, but they are

rather similar in a general way, and it is the opinion of Dr. Ramberg that they may be considered to be derived from similar sedimentary rocks. Present differences are thus due to metasomatism. Whatever the origin of the rocks, they have been metamorphosed so that S 110 and 111 are in the amphibolite facies, and the remainder in the granulite facies.

The average thallium content of S 110 and 111 is 0·91 ppm, and for S 70, 33, 32 and 34 is 0·16 ppm. If these figures are representative, which is by no means certain, and if the rocks were all derived from similar sediments, one must conclude that in this case increasing metamorphism has decreased the thallium content. This would be the opposite effect from what was found in the Dutchess County schists, and seems to imply a removal of thallium in the highest grades of metamorphism. These apparently opposite trends cannot be reconciled at the present, whilst they are founded on such meagre figures. The whole field of trace-elements in metamorphism is almost untouched, and very worthy of study.

## General Conclusions

### *Crustal abundance of thallium*

It is highly probable that the earth has evolved from materials of meteoritic composition. This has been a popular hypothesis for a century, and recent work by Brown and Patterson [10], founded on Goldschmidts earlier studies, has shown the theory to be in substantial agreement with the interpretation of meteorite chemistry along thermo-dynamical lines. Thallium was not detected in any of the meteorites analysed here, and so it is still not possible to compute a cosmic abundance.

The early evolution of the earth gave rise to a crust rich in silica, alumina, alkalies, and lime, with a composition rather similar to quartzdiorite. From this crust the earliest sediments were formed by weathering and transportation. The present crust is thus derived entirely from igneous rocks, in the first place, excepting material added by volcanic emanations. The quantity of thallium in the latter category is negligible (see later), and we can therefore assume that the average thallium content of igneous rocks will give a representative figure for the crust as a whole.

It has been customary in the past to take the average igneous rock as calculated by Clarke and Washington [11] to be representative. By their procedure, one finds the average abundance of an element by taking the arithmetic mean of a large number of analyses of igneous rocks. A number of writers (*e.g.* Sederholm, Knopf, Vogt) have pointed out, however, that the relative abundance of the different rock types must be taken into account. Thus in the following calculation (Table 7), the arithmetic mean of the thallium contents of each rock type has been taken from Table 3, and this mean is then multiplied by a weight-factor expressing the relative areal abundance of that rock type. The abundances refer to certain large areas in the Western U.S.A. and the Appalachian belt, as measured by Daly [12] and grouped by Knopf [30]. Certain of Knopfs minor rock groups have been combined under one heading. By contrast the average abundance of thallium obtained by taking the arithmetic mean of the same igneous rocks is 1·41 ppm, a figure which is some 8% higher, reflecting the fact that a relatively large number of granites were analysed.

It is appropriate to consider some earlier figures for the crustal abundance of thallium. I. and W. Noddack gave the low figures of 0·1 ppm [38] and 0·01 ppm [39].

*Table 7. Thallium content of the mean igneous rock*

| *Rock type* | *Number of Samples* | Tl *mean ppm* | *Abundance factor* | *Weighted thallium Mean ppm* |
|---|---|---|---|---|
| Diorite and Andesite . . . . | 2 | 0·15 | 0·255 | 0·0382 |
| Granite . . . . . | 10 | 3·1 | 0·230 | 0·7130 |
| Basalt. . . . . | 4 | 0·124 | 0·206 | 0·0255 |
| Rhyolite Obsidian . . . . . | 2 | 3·5 | 0·127 | 0·4445 |
| Granodiorite, etc. . . . . | 4 | 0·43 | 0·126 | 0·0541 |
| Gabbro . . . . . | 6 | 0·135 | 0·038 | 0·0051 |
| Syenite and Monzonite . . . | 3 | 1·4 | 0·008 | 0·0112 |
| Peridotite and Pyroxenite . . | 4 | 0·06 | 0·004 | 0·0002 |
| Anorthosite . . . . . | 2 | 0·015 | 0·003 | 0·0000 |
| Nepheline Rocks . . . . . | 3 | 3·6 | 0·001 | 0·0036 |
| Total . . . . . | | | | 1·2954 |

Mean crustal abundance of thallium = 1·30 ppm.

These figures are very much too low, and Goldschmidt [18] estimated the value to be 0·3 ppm.

Arguing from the constancy of the Rb/Tl ratio in pegmatitic minerals Ahrens [4] estimated the crustal abundance to be 3 ppm. Rankama [47] criticised the validity of Ahrens' method, suggesting that the value 0·6 ppm would be closer to the truth.

Novokhatskii and Kalinin [41] state that the ratio Tl/K for the crust of the earth is equal to 1/86, 700. Taking the potassium content of the average igneous rock as 25900 ppm (Clarke and Washington [11]), the crustal abundance of thallium would then be 0·3 ppm. However it will be shown in the next section that the Tl/K ratio is larger than 1/86700 in both basic and silicic rocks.

The rule of Oddo and Harkins states that the abundance of an element of even atomic number should be greater than its adjacent neighbours of odd atomic number. Rankama [47] has discussed the validity of this rule in respect of mercury, thallium and lead. Thallium (A.N. 81) is less abundant than lead (A.N. 82) but more abundant than mercury (A.N. 80). The low crustal abundance of mercury (0·077–0·5 ppm) is caused by its extreme volatility and consequent loss from the earth in pre-geological times. The new abundance figure for thallium in no way affects this argument, beyond showing that mercury deviates more strongly than was apparent from the rule of Oddo and Harkins.

In the above discussion the chalcophile behaviour of thallium can be neglected, since this is quantitatively insignificant.

### *Rubidium-thallium ratios*

The rubidium-thallium ratio has been mentioned frequently in the preceding pages. Ahrens showed that the ratio of rubidium to thallium in a large number of pegmatite mineral specimens has a relatively constant value. Ahrens made 167 analyses of potash feldspars, albitic plagioclase feldspars, micas and pollucites, and demonstrated that although the $Rb_2O/Tl_2O$ values lay between the extremes of 12 and 650 they are grouped statistically about a mean value of 90 ([5], p. 585). This indicates that under pegmatitic conditions rubidium and thallium show very close geochemical coherence, in a manner similar to zirconium and hafnium. Ahrens

assumed that this ratio can be extended to all igneous rocks, and thereby calculated the crustal abundance of thallium to be 1/100 of the abundance of rubidium, or 3 ppm*.

This assumption has been discussed and criticised by Rankama [47] with the aid of a few determinations by Goldschmidt [18], Otteman [43], and Preuss [45]. The fundamental question is whether this close coherence of rubidium and thallium holds for all igneous rocks, as well as for the pegmatitic stage of crystallisation. In Table 8 some relevant figures are assembled. Thallium values are from the present work, whilst other analyses are taken from the literature cited. With respect to the Finnish granites it should be pointed out that thallium analyses were not made on the same samples as rubidium. The abbreviation "vis" of course denotes that the analyses were estimated by visual comparison and so are only semi-quantitative. The final average Rb/Tl ratio for all granites takes into account the figures on the second line of the table.

It is apparent from Table 8 that thallium and rubidium do in fact show the very close geochemical coherence which Ahrens has stressed. But it is equally clear that the average Rb/Tl ratios are substantially different in gabbros, granites and pegmatites, thus accounting for the high figure for the crustal abundance of thallium, as calculated by Ahrens. Moreover the granites have a higher ratio than either the gabbros or the pegmatites, although it is clear from the two ratios for the Salmi granite that individual ratios are of little value, and only the mean is of value for comparison.

The reason why the igneous rocks fail to preserve the constant Rb/Tl ratio is difficult to find. The coherence of rubidium and thallium is due to their identical atomic radii (1·49 Å) in the univalent state, and these elements certainly show remarkably similar behaviour in all igneous rocks. Both are camouflaged by potassium (radius 1·33 Å), and the radius difference explains their low abundance in basic rocks. For first of all potassium itself is at a low concentration, and secondly the potassium is mostly present in high temperature feldspars which cannot take up an appreciable quantity of the much larger ions of rubidium and thallium. Thus the ratio K/Tl decreases markedly during evolution of the igneous rocks, as shown in the above table. Crystal chemistry does not, however, appear to give any reason for the behaviour of the Rb/Tl ratio. If the ratio varied consistently one might well conceive of a polarisation of the much heavier thallium ion. But the ratio appears to rise, then fall again. This would imply a loss of thallium (relative to rubidium) at the granite stage of differentiation. At least two explanations seem possible.

Firstly, it is possible that granites are not produced by the differentiation of basic magmas, and hence the only comparable figures are those for granites and pegmatites, which presumably are co-genetic. The differentiation of granite magma or emanations might then give rise to an enrichment in thallium in the pegmatites, or a lower Rb/Tl ratio. The petrology of this could be explained by any one of the current views except the origin of granite by basalt differentiation.

The other explantion involves the chalcophile tendencies of thallium. Assuming a magmatic origin for granites, it is probable that at the granitic stage of differentiation the volatile magmatic constituents attain a large concentration (say 10%

* Ahrens' oxide ratio is 90, which would give a metal ratio of 85, rather than 100. With a rubidium abundance of 300 ppm this would give a thallium abundance of 3·5 ppm.

*Table 8. Potassium, rubidium, thallium values*

| *Rock* | K *ppm* | $Rb_2O$ *ppm* | Rb *ppm* | Tl *ppm* | K/Tl | Rb/Tl |
|---|---|---|---|---|---|---|
| Gabbro and Basalt (average) | 7400** | | 18** | 0·13 | 56900 | 138 |
| Granite (average) | 33800** | | 830† | 3·1 | 10900 | 268 |
| Granite Pegmatite minerals | | | | | | 95* |
| Orijärvi granite | | 300†† | | 0·42 | | 653 |
| Hangö granite | | 1600†† | | 6·4 | | 229 |
| Bodom granite | | 1100†† | | 4·8 | | 209 |
| Marianvaara granite | | 1100†† | | | | |
| Marianvaara granite | | 800†† | | | | |
| Marianvaara granite (mean) | | 950†† | | 1·7 | | 512 |
| Salmi granite (Uuksu) | | 2000†† vis. | | 3·0 | | 609 |
| Younger granite of S. Lapland (Nattanen type) | | 2000§ vis. | | | | |
| Younger granite of S. Lapland (Nattanen type) | | 2000§ vis. | | | | |
| Younger granite of S. Lapland (Nattanen type)' | | 1000§ vis. | | | | |
| Younger granite of S. Lapland (Nattanen type) | | 1000§ vis. | | | | |
| Younger granite of S. Lapland (Nattanen type) (mean) | | 1500§ vis. | | | | |
| Mixture of younger granites of Nattanen type | | 1000§ vis. | | 1·5 | | 609 |
| Salmi granite | | 1000§§ vis. | | | | |
| Salmi granite | | 900§§ | | | | |
| Salmi granite | | 1200§§ | | | | |
| Salmi granite (mean) | | 1030§§ | | 3·0 | | 315 |
| Mixture of Rapakivi granites | | 1600§§ | | | | |
| Mean of three Rapakivi granites | | (1600) | | 3·3 | | 443 |
| Average for all Finnish granites | | 1200 | 1100 | 3·0 | | 370 |
| Average for all granites | | 1160 | 1060 | 3·1 | | 340 |

* Ahrens' oxide ratio is 90 which would give a metal ratio of 85 rather than 95. With a Rb abundance of 300 ppm this would give a Tl abundance of 3·5 ppm.

** Goldschmidt, Bermann, Hauptmann and Peters [20].

† Goldschmidt, Bauer and Witte [21].

†† Erämetsä, Sahama and Kanula [13].

§ Sahama [53].

§§ Sahama (54).

$H_2O$ by weight) and commence to boil away and disperse themselves in surrounding country rock, giving rise to hydrothermal phenomena. These solutions are believed to carry many heavy elements, later deposited as sulphides. It is probable that thallium will distribute itself across this two-liquid or liquid-fluid system, thereby empoverishing the granite to some extent, and at the same time accounting for the occurrence of thallium in many sulphide ores. On the other hand rubidium would have no such tendency. Assuming that the silicate magma and hydrous fluids are more or less independent after this initial separation, further consolidation of granite would give rise to a thallium enrichment in the pegmatite magma. Although this second hypothesis is attractive, it does not explain the low Rb Tl ratio in pegmatites.

*Geochemical balance*

It is informative to consider the quantitative distribution of thallium between igneous rocks on the one hand, and their products of erosion on the other. Goldschmidt first calculated the sodium balance [16] evaluating the relative quantities of the materials concerned as follows:

| | |
|---|---|
| Mass of the oceans | = 278 kg/cm² of the earth's surface |
| Mass of the average igneous rocks | = 160 kg/cm² |
| Mass of the average clay and sandstone sediments | = 155 kg/cm² |

If the average concentrations of thallium in these three materials are $z$, $x$ and $y$, respectively, then the following equation should hold:

$$160\,x + 155\,y = 278\,z\,.$$

If we neglect $z$, which is extremely low, we obtain:

$$160\,x = 155\,y\,.$$

Using the figure $x = 1{\cdot}30$ ppm we find that $y = 1{\cdot}34$ ppm. Pettijohn [44] estimates the relative proportions of clay, sandstone and carbonates to be 58:22:20. We can neglect the carbonates again, so that if $v$ and $w$ are thallium contents of clay and sandstone respectively we find that

$$\frac{58}{80}\,v + \frac{22}{80}\,w = 1{\cdot}34\,.$$

Using the figure $v = 0{\cdot}69$ ppm (Table 5) then we find that $w = 3{\cdot}1$ ppm.

Now the actual value of $w$ must probably lie between 0·88 ppm and 2·0 ppm (Table 5). This implies that either the values are not representative, or that thallium is present elsewhere in the sediments. The latter is more likely to be correct, and it is probable that a considerable quantity of thallium is precipitated in the strong oxidising environment of the manganese sediments, which of course are not considered in the preceding calculations.

In this connection it is interesting to calculate the Rb/Tl ratio in clay sediments. Using the thallium content as 0·69 ppm and the rubidium content as 300 ppm (Goldschmidt, Bauer and Witte [21]), the Rb/Tl ratio is 435. This figure shows the impoverishment of thallium in clays, and its separation from rubidium in the exogenic cycle, due to different behaviour under oxidising conditions.

It is seen that there is no suggestion of more thallium being present in sediments and the oceans than is available from the weathering of igneous rocks, and hence little can have been added to the lithosphere and hydrosphere by volcanic emanations.

*Petrological aspects*

The preceding discussion has several times touched upon the fundamental problem of petrology,—whether all the so-called igneous rocks are of magmatic origin. Since the distribution of thallium in these rocks is governed by their history, some further discussion is necessary.

It has been seen that the theories of magmatic differentiation explain the distribution of thallium in igneous rocks very well, by the concepts of crystal chemistry. The rubidium-thallium ratios show an inconsistency however, suggesting some special circumstances in the formation of granites, which may be connected with

the separation of the ore-forming fluids. In addition there is some evidence that in one area the metamorphism of shales has been accompanied by a slight addition of thallium by metasomatism. Continued alteration of these shales gave rise to granitic gneisses.

Various regenerative processes have been suggested to account for the origins of granite. The geochemical behaviour of thallium seems consistent with some of these theories. Thus a metasomatic addition of thallium would be necessary during the alteration of shale to granite by recrystallisation. Alternatively the differential anatexis of shales would give a partial magma enriched in thallium for the same crystal chemical reasons that it is enriched in the residual magma from magmatic differentiation.

In discussing the geochemistry of tantalum, RANKAMA [46] shows how the accepted modes of origin of Finnish granites are in full accord with the interpretation of certain trace element contents. SEDERHOLM [58] classifies the granites of Finland in four main groups, according to age. The earliest (Group I) are believed to be of mainly magmatic origin, whilst Groups II and III were formed by successive re-fusion of the earlier granites. Group IV comprise the late-pre-Cambrian Rapakivi intrustions. The representative samples analysed here are presented in Table 9.

*Table 9. Thallium contents of Finnish granites*

| *Sample* | *Rock* | *Locality* | *Group* | *ppm* Tl |
|---|---|---|---|---|
| S 56 | Granite | Orijärvi Kisko | I | 0·42 |
| S 52 | Granite-Gneiss | Petäjäkylä, Pitkärantä | I | 2·8 |
| S 114 | Granite | Hangö | II | 6·4 |
| S 53 | Granite | Juva (Bodom type) | III | 4·8 |
| S 49 | Granite | Sodankylä (Nattanen type) | III | 1·5 |
| S 54 | Granite | Åva Brändö (Åva type) | III | 2·3 |
| S 51 | Granite | Maarianvaara | III | 1·7 |
| S 55 | Granite | Bomarsund Ahvenanmaa, | IV | 4·0 |
| S 48 | Granite | Uuksu, Salmi | IV | 3·0 |
| S 50 | Granite | Bambole, Vehkalahti | IV | 2·8 |

The mean values for Groups III and IV are 2·6 ppm and 3·3 ppm respectively.

A line of reasoning similar to that of RANKAMA (*op.cit.*) can be adopted. Thus if the differential anatexis of Group I granites has produced those of Group II the thallium contents agree with this hypothesis. For the melt produced by selective re-fusion would be enriched in low-melting components, as discussed above, and the resulting granite, exemplified by the Hangö type, is rich in thallium. The relation does not however apply to the supposed origin of Group III granites by selective fusion of Group II types, unless the anatexis had gone a stage further to produce a more intermediate or granodioritic magma.

## SUMMARY

It is now possible to summarise the geochemistry of thallium, in the light of the previous discussions.

The thallium content of meteorites is extremely low. During the primary earth differentiation thallium migrated towards the crust, along with the alkali metals.

Assuming the processes of igneous differentiation to operate, thallium is present in parental mafic magmas to the extent of about 0·13 ppm. Early ultra-basic rocks contain very little thallium, and as differentiation proceeds the element is enriched in later magmas, as is the case for rubidium, which has the same ionic size and valency. Both elements are camouflaged in potassium minerals, with thallium remaining almost entirely in the univalent state. Granites contain about 3·1 ppm and thallium does not rise to any noteworthy abundance until the lower temperature pegmatite silicates are formed, when up to 100 ppm are present in micas and potash-feldspars. During the separation of the ore-forming fluids a certain amount of thallium is carried in solution, and is eventually deposited in unknown quantities in several common sulphides such as galena and sphalerite. Also some thallium is deposited in fumarolic activity.

During erosion and transportation thallium goes into solution as the univalent cation. Under strong oxidising conditions it is deposited in manganese-rich sediments and any remaining in solution is almost completely adsorbed in clay sediments. Some remains in arenaceous sediments rich in alkali feldspar. A strong reducing environment also concentrates thallium to a limited extent, so that carbonaceous shales are slightly enriched. Very little thallium can be present in ocean water, although some is extracted by marine organisms.

Little is known of the behaviour of elements during metamorphism, but there is some evidence in one case that during the metamorphism of pelitic sediments a little thallium was added from outside in the higher zones.

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